## REMARKS

Applicants and Applicants' attorney would like to thank Examiner Dang for his patience and guidance in the interview of May 25, 2004. Claims 2, 9 and 13 are cancelled herewith, as well as claims 22-26, previously withdrawn in the restriction requirement. Pending claims now include Claims 1, 3-8, 10, 12, 14 and 15. Minor amendments have been made to other claims to correct claim dependencies in view of the cancellation of Claim 2.

### Rejections Under 35 USC § 103

Claims 1-10 and 12-15 were rejected under 35 USC § 103(a) as being unpatentable over Gi (4,463,203) in view of either Roy (4,740,270) or Solbakken et al. (4,250,158). Claims 2, 9 and 13 have been incorporated into Claim 1, and these claims cancelled. Claim 1 has also been amended to recite "clay catalyst", and "carbon black" in place of "solid carbonaceous residue". The combination of references cited does not teach or suggest the invention recited in Claim 1.

As requested by the Examiner, Applicants submit herewith the following references 1) "Catalytic Cracking with an Interlayered Clay. A Two-Dimensional Approach", Ocelli, M.L., *Ind. Eng. Chem. Prod. Res. Dev.* 1983, 22, 553-559; and 2) pages from Volume 4 of the Kirk-Othmer Encyclopedia of Chemical Terminology, 4th Ed., Wiley & Sons, 1998.

Reference (1) describes the ability of pillared clay to act as a catalyst, and notes on page 1, in the paragraph entitled "Conclusions and Significance", that above temperatures of 620°C, the clay becomes unstable, and higher temperatures cause a drastic reduction in the clay's catalytic activity. This reference thus provides support for Applicants' position that the clay used by Gi is probably not functioning as a catalyst (indeed, it is not described therein as a catalyst) because of the high temperatures used by Gi.

Reference (2) provides a complete description of the carbon black, and describes on page 1037 distinctions that can be made between carbon black and other forms of carbon such as diamond, graphite, coke, and charcoal: carbon blacks are distinct because they are "particulate, composed of aggregates having complex configurations,

quasigraphitic in structure, and of colloidal dimensions". Applicants' method releases carbon black from the rubber tires, whereas the method of Gi produces coke.

Applicants respectfully submit that the claimed invention is patentable over the Gi reference, alone or in combination with Roy or Solbakken. As all outstanding issues have been addressed, Applicants submit that Claims 1, 3-8, 10, 12, 14 and 15 are in condition for allowance; such action is respectfully requested at an early date.

Respectfully submitted,

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# Catalytic Cracking with an Interlayered Clay. A Two-Dimensional Molecular Sieve

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The interlayering of commercial bentonite with aluminum hydroxy cations $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ produces an expanded clay with surface area, pore volume, and pore size distribution more typical of zeolites than of clays. Spectroscopic studies with chemisorbed pyridine have shown that the interlayered clay contains both Bronsted and Lewis acid sites. At high temperature (400 °C under vacuum), acidity was found to be mostly of the Lewis type. When tested for microactivity under mild pretreatment conditions, interlayered clays were found to be as active as a commercial cracking catalyst containing zeolite. However, if the cracking activity evaluation is performed under typical pilot plant conditions, the interlayered clay loses its surface area and most of its catalytic activity.

## Scope

In the United States, one-third of all processed crude oil, amounting to about $5 \times 10^6$ bbl/day, is catalytically converted over fluidized catalysts. Over 400 tons of catalyst are required daily, yielding sales which in 1982 were estimated at ~376 million dollars (*Oil Gas J.* Nov 1982, 28). Thus, in terms of catalyst usage and product value, catalytic cracking is the most important unit operation of the petroleum refining industry. In a typical fluid catalytic cracking (FCC) unit, oil is contacted and vaporized by the hot fluidized catalyst in either the feed riser line or in the reactor. Cracking occurs in the riser at temperatures between 480 and 520 °C. Catalyst and cracking products are mechanically separated, and occluded oil on the catalyst surface is removed by steam stripping at 500–540 °C. Catalyst regeneration is completed by burning off coke deposits in controlled air at temperatures in the 600–700 °C range in the presence of small amounts of water. Then, from the regenerator, the catalyst flows into the incoming oil for reutilization (Figure 1). Catalyst stability at the thermal and hydrothermal conditions required for regeneration is essential for the maintenance of high activity and is critical in determining the commercial importance of a cracking catalyst.

Vaughan et al. (1979) have reported that interlayered clays can be used as zeolite-free cracking catalysts. Lussier et al. (1980) have published pilot plant and microactivity data, indicating that interlayered clays are less active than zeolite-based catalysts but more selective with respect to light cycle gas oil (LCGO) generation. Recently, Occelli and Tindwa (1982) have studied the physicochemical properties of these catalysts and reported that bentonite interlayered with aluminum oligomers contains both Bronsted and Lewis acid sites, and that between 540 and 760 °C, the pillared structure collapses with a corresponding decrease in surface area and catalytic activity. It is the purpose of this paper to further explore the thermal and hydrothermal stability of an interlayered clay mineral and explain its catalytic activity in terms of surface properties.

## Conclusions and Significance

The interlayering of commercial calcium bentonite with aluminum hydroxy cations $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ produces an expanded clay structure having a surface area of ~270 m²/g thermally stable to 500 °C. Between 500 and 700 °C, a partial collapse of the structure occurs. After heating in air at 700 °C, for 10 days, the pillared clay

retained ~64% of its original surface area. In a stream of 95% steam and 5% nitrogen, the interlayered clay is stable up to 620 °C. Above 620 °C, stability becomes a function of time and after 8 h at 675 °C or 4 h at ~730 °C, there is a drastic reduction of surface area, pore volume, and catalytic properties. When tested for cracking activity after mild hydrothermal pretreatment conditions, interlayered clays are as active as several commercial catalysts containing zeolites in converting a gas oil having a 260–426 °C boiling range and a "*K*" factor of 12.02. At conversion levels in the range of 60–80%, the interlayered clay exhibits a higher coke make, but better selectivity with respect to light cycle oil formation than the commercial cracking catalysts tested. At high (~78%) conversion, both catalysts give similar gasoline yields (~61%). Spectroscopic studies of chemisorbed pyridine have revealed that an interlayered calcium bentonite contains both Bronsted and Lewis acid sites and that at test conditions, (in vacuo), acidity is probably mostly of the Lewis type. Under actual cracking conditions, both types of sites are likely to be present. The nature of the acid sites and the ease with which $C_6$–$C_{10}$ n-paraffins and branched aromatics can be sorbed and diffused is believed to be responsible for the cracking activity and product selectivity of interlayered clays.

## Introduction

Catalytic cracking has been and is the major process for gasoline manufacture. Prior to 1938, gasoline was obtained from thermal cracking plants; then fixed-bed catalytic cracking led to the development of a fluid process by Standard Oil for the catalytic production of motor fluids (O'Dell, 1934; Hemminger, 1942; Brueckmann, 1942; Gohr et al., 1943; Tyson, 1943). Acid-treated clays of the montmorillonite type were the first fluid cracking catalysts widely employed by the industry. Thomas (1949) distinguished between weakly acidic structural hydrogen ions and the strongly acidic hydrogen ions of the type produced by hot acid treatment of the clay. Early work of Thomas et al. (1950) showed that only the latter hydrogen contributed to catalytic activity and confirmed that cracking takes place by a carbonium ion mechanism. By the end of World War II, clays were abandoned in favor of synthetic silica–alumina, silica–magnesia, alumina, or even phosphate catalysts (Marshall, 1952). Then, in the early sixties, the catalytic properties of synthetic faujasite were discovered and zeolites rapidly came to dominate the petroleum refining industry. In 1976, the first African fluid
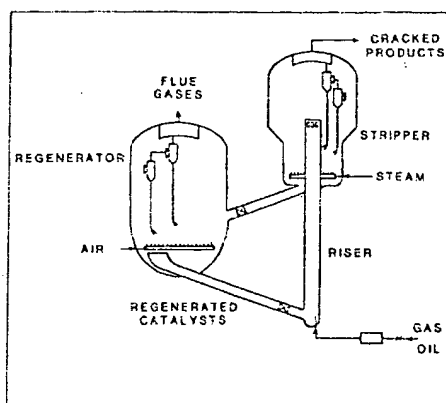
Figure 1. Fluid catalytic cracking (FCC) unit configuration.

Table I. Chemical Analysis

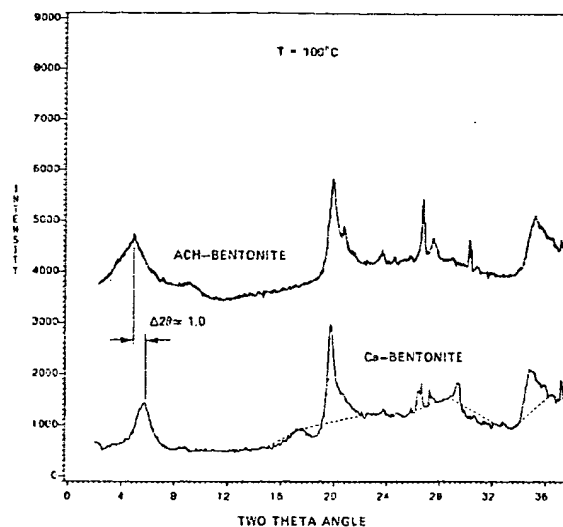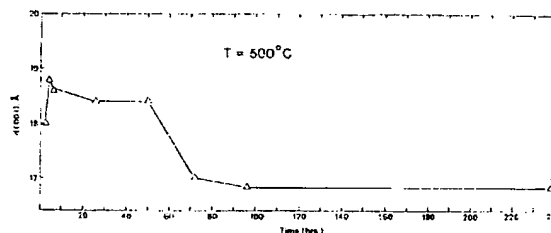| wt % | bentonite | pillared bentonite |
|---|---|---|
| $Al_2O_3$ | 15.25 | 26.20 |
| $SiO_2$ | 56.17 | 54.49 |
| $Fe_2O_3$ | 4.87 | 4.65 |
| $Na_2O$ | 0.70 | 0.39 |
| $K_2O$ | 0.88 | 0.75 |
| MgO | 2.77 | 2.44 |
| CaO | 3.24 | 0.14 |
| $H_2O$ | 15.54 | 10.10 |
| | 99.42 | 99.16 |



Figure 2. X-ray diffractograms of Ca-bentonite before and after interlayering with aluminum chlorohydroxide (ACH) polymer.



Figure 3. Basal spacing, $d(00l)$, of a pillared Ca-bentonite as a function of time when heated at 500 °C in air.

cracking unit became operational in Nigeria and since then all of the catalytic cracking in North America and the USSR employed zeolites (Vaughan, 1979; Dorogochinskii, 1975).

After 40 years, clays have once more come to the attention of the refiners because zeolite-like materials have been synthesized by interlayering expandable clay minerals with oligomeric molecules derived from the hydrolysis of polyvalent cations such as $Al^{3+}$ and $Zr^{4+}$ (Brindley and Sempels, 1977; Lahav et al., 1978; Yamanaka and Brindley, 1979; Vaughan et al., 1979; Shabtai et al., 1980; Lussier et al., 1980).

Experimental Section

Catalyst Preparation. The starting material was a calcium-rich bentonite obtained from the American Colloid Co. which X-ray analysis showed to contain 95% montmorillonite and minor amounts of quartz, K-spar, calcite, and pyrite impurities. Its chemical composition is shown in Table I. Bentonites can be readily ion exchanged with hydroxy aluminum oligomers by first slurrying the clay in water and then by adding the polymer. After 1 h at 90 °C, the exchange is essentially complete. The slurry is then filtered, washed, and oven-dried at 120 °C overnight. The exchange reaction typically increases the surface area of the clay from 50 $m^2/g$ to ~270 $m^2/g$ and generates an expanded structure with a basal spacing of ~18.2 Å and pore volume in the range of 0.16–0.22 $cm^3/g$.

The hydroxy aluminum oligomer used was a basic aluminum chloride salt marketed by the Reheis Chemical Co. under the tradename of Chlorhydrol. The structure of this salt is still being debated. Johansson (1960) has proposed $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, a cation consisting of a four-coordinated aluminum atom surrounded by 12 $AlO_4$-octahedra joined together by common edges.

Surface Characterization. The Barrett–Joyner–Halenda (1950) method has been used to calculate pore size distribution from nitrogen adsorption isotherms. The

value of adsorbed gas V at 64 relative pressures, $P/P_0$, in the range of 0.046 to 0.967 has been used for this purpose. Infrared measurements were performed on a Nicolet 7000 FTIR spectrometer. X-ray powder patterns were recorded by a standard Phillips diffractometer equipped with a pulse height analyzer, using Cu $K\alpha$ radiation; $\alpha$-$Al_2O_3$ was used as the internal standard.

Catalyst Testing. Catalytic evaluation was performed by use of a microactivity test (MAT) similar to the one described by Ciapetta and Anderson (1967). The weight hourly space velocity was 15, with an 80 s catalyst contact time at 515 °C. A catalyst-to-oil ratio of 2.5 was used. The charge stock was a gas oil having a 260–426 °C boiling range (see Table II). Steam deactivation of the interlayered clay was accomplished by passing a mixture of 95% steam and 5% nitrogen for different periods of time using temperatures in the 565–730 °C range. All reference commercial catalysts tested contained an estimated 20–30% zeolite with the Faujasite structure and were steam deactivated either at 730 °C for 10 h or at 815 °C for shorter periods of time.

Results

Interlayered Clay Thermal Stability. In Figure 2, a typical X-ray diffractogram showing the $d(00l)$ peak for a bentonite before and after pillaring with aluminum oligomers is given. The observation of temperature effects on the $d(00l)$ spacing is a convenient way to investigate the thermal stability of an interlayered clay (Figure 3). These results indicate that the pillared clay is thermally stable to 500 °C. Heating at 600 and 700 °C caused a partial collapse of the interlayered structure. After 10 days at 700 °C in air, the interlayered clay retained, nonetheless,
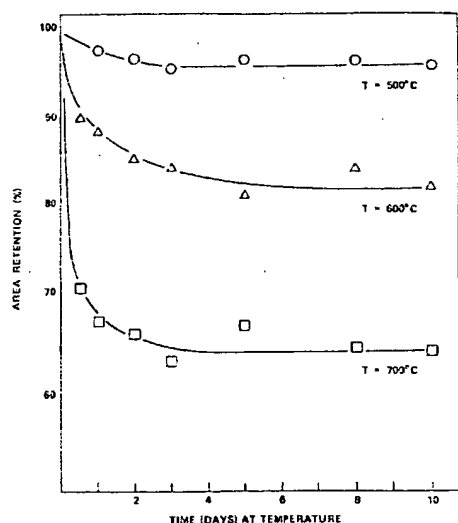
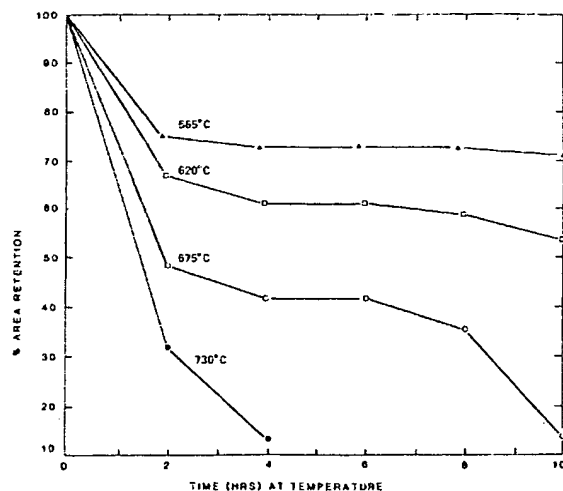Figure 4. The thermal stability of ACH-bentonite in air.



Figure 5. Hydrothermal treatment effects on a pillared calcium bentonite surface area.
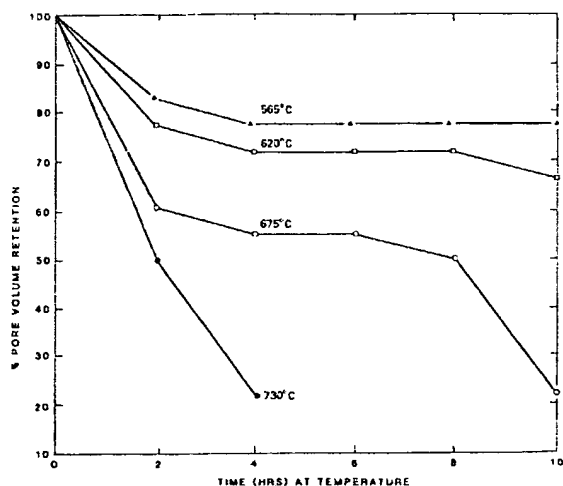


Figure 6. Hydrothermal treatment effects on a pillared calcium bentonite pore volume.

Table II. Charge Stock Inspections

| feed | Cincinnati gas oil |
|---|---|
| gravity:  API | 27.9 |
| sulfur, wt % | 0.59 |
| nitrogen, wt % | 0.0946 |
| carbon residue, wt % | 0.33 |
| hydrogen, wt % | 12.72 |
| viscosity, 210 °F | 40.9 |
| pour point, °F | +100 |
| nickel, ppm | 0.3 |
| vanadium, ppm | 0.3 |
| vacuum distillation, °F | |
| 10% at 760 mm | 595 |
| 30% | 685 |
| 50% | 765 |
| 70% | 845 |
| 80% | 934 |

Calc. Carbon Type Compositions

| vol. fraction | |
|---|---|
| aromatic | 0.155 |
| naphthenes | 0.217 |
| paraffins | 0.627 |

Hydrocarbon Type

| aromatics (mass spec) | 32.2 | |
|---|---|---|
| mono | | 11.8 |
| di | | 10.9 |
| tri + | | 9.5 |
| saturates | 61.7 | |
| polar compounds | 0.8 | |
| Watson K factor | 12.02 | |

64% of its initial surface area (see Figure 4).

The effect of time on the hydrothermal stability of an interlayered clay in shown in Figure 5. In the presence of a mixture of 95% steam and 5% nitrogen, the pillared clay hydrothermal stability is limited to temperatures that do not exceed 620 °C. Above 620 °C, the structure can

be collapsed either by heating at 675 °C for 10 h or by heating at 730 °C for 4 h. Figures 5 and 6 show that as the pillars decompose, a progressive decrease in pore volume and surface area occurs until these surface properties are reduced to that of the clay prior to interlayering (Tables III and IV).

Catalytic Properties. The catalytic properties of an interlayered clay are dependent on the method of hydrothermal deactivation used to simulate the state of an equilibrium catalyst. While most of the commercial catalysts tested were found to be hydrothermally stable to 730 °C, Figure 7 shows that the activity of the interlayered clay studied strongly depends both on steaming temper-

Table III. Steaming Effects on a Pillared Calcium Bentonite Microporous Structure for $T \leqslant 620$ °C

| steaming $T$, °C: | 565 °C | | | | 620 °C | | | |
|---|---|---|---|---|---|---|---|---|
| pore radius, A: area % at time, h | <10 | 10 < R < 15 | 15 < R < 20 | >20 | <10 | 10 < R < 10 | 15 < R < 20 | >20 |
| 0 | 87.8 | 6.8 | 2.2 | 3.2 | 87.8 | 6.8 | 2.2 | 3.2 |
| 2 | 84.4 | 7.8 | 2.6 | 5.2 | 77.8 | 11.2 | 3.9 | 7.1 |
| 4 | 79.4 | 10.9 | 3.5 | 6.2 | 75.1 | 13.3 | 3.9 | 7.7 |
| 6 | 83.2 | 8.9 | 2.8 | 5.1 | 78.2 | 10.6 | 3.8 | 7.4 |
| 8 | 81.8 | 9.9 | 3.0 | 5.3 | 74.8 | 12.7 | 4.4 | 8.1 |
| 10 | 82.3 | 9.1 | 3.1 | 5.5 | 69.7 | 15.4 | 5.3 | 9.6 |

Table IV.  Steaming Effects on a Pillared Calcium Bentonite Microporous Structure for $650 < T < 750\,°C$

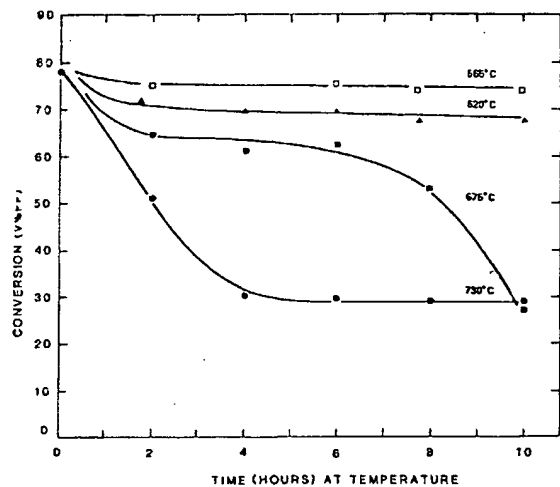| steaming $T$, °C: | 675 °C | | | | 730 °C | | | |
|---|---|---|---|---|---|---|---|---|
| pore radius, A: area % at time, h | <10 | $10 < R < 15$ | $15 < R < 20$ | >20 | <10 | $10 < R < 15$ | $15 < R < 20$ | >20 |
| 0 | 87.8 | 6.8 | 2.2 | 3.2 | 87.8 | 6.8 | 2.2 | 3.2 |
| 2 | 69.6 | 14.6 | 5.4 | 10.4 | 52.9 | 21.7 | 7.9 | 17.5 |
| 4 | 66.1 | 15.8 | 5.7 | 12.4 | 28.6 | 20.4 | 10.1 | 40.9 |
| 6 | 65.9 | 15.4 | 5.4 | 13.3 | -- | -- | -- | -- |
| 8 | 58.5 | 19.9 | 6.9 | 14.7 | -- | -- | -- | -- |
| 10 | 29.3 | 20.8 | 9.5 | 40.4 | -- | -- | -- | -- |



Figure 7.  Hydrothermal treatment effects on a pillared calcium bentonite cracking activity.



Figure 9.  Light cycle gas oil yields.
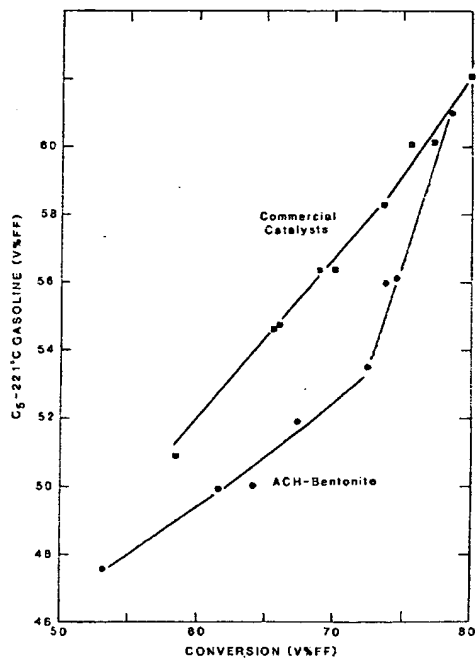


Figure 8.  Gasoline yields.



Figure 10.  Slurry oil yields.

ature and time.  In Figures 8–16, selectivity data are compared with one of the commercial catalysts with different activity and indicate that interlayered clays yield less gasoline, less slurry oil (343 °C) and more light cycle gas oil (LCGO) (221–343 °C) than typical zeolite-based cracking catalysts.  At high conversion, the gasoline make of ACH-bentonite approaches that of the commercial

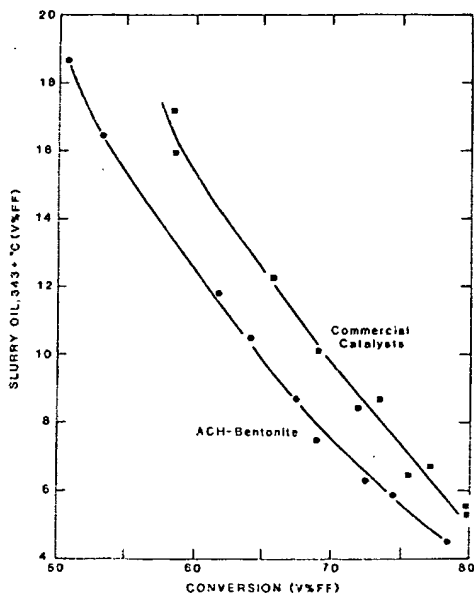catalyst having similar activity but it retains its LCGO selectivity advantage.  Higher light gas make ($C_1 + C_2$), hydrogen, and coke generation have been observed over the entire conversion range investigated.  Saturates (i.e., $C_3$ and $C_4$) and olefins yields in Figures 11–13 indicate
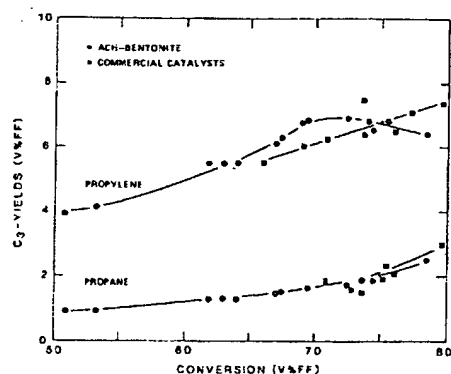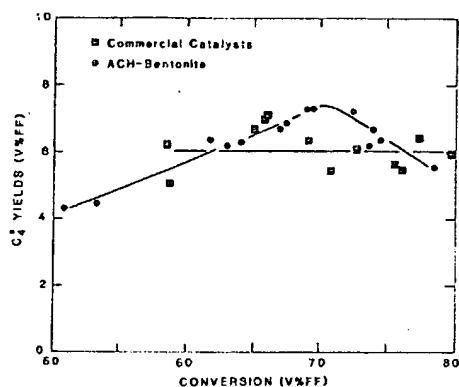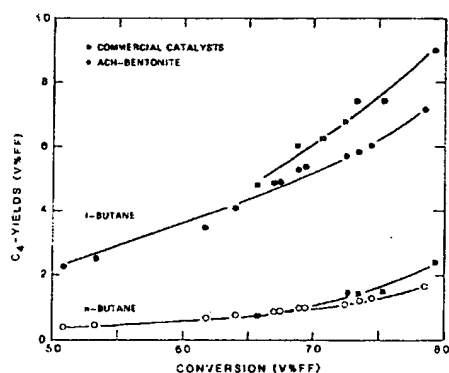
Figure 11. C₃ yields.
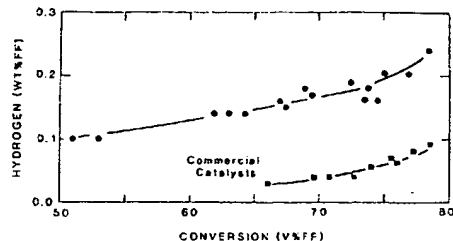


Figure 12. Butenes yields.



Figure 13. Butanes yields.



Figure 14. Hydrogen yields.
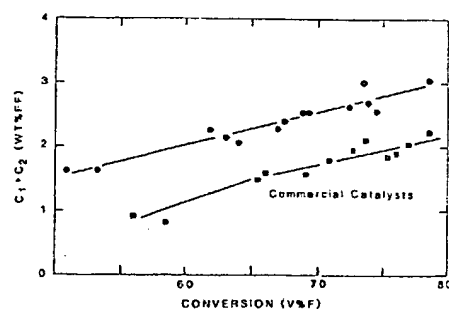


Figure 15. $C_1 + C_2$ yields.
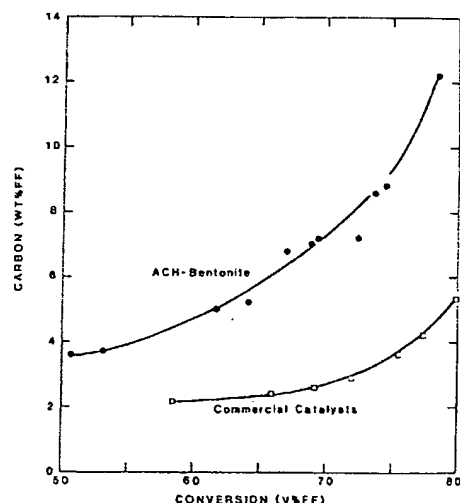


Figure 16. Carbon yields.

tonically increase with conversion while $C_4^=$ yields stay essentially unchanged at ~6%.

**Discussion**

By exchanging the $Ca^{2+}$ and $Na^+$ ions in a bentonite with aluminum hydroxy cations, an expanded clay mineral is obtained, characterized by a pore volume of 0.18 $cm^3/g$ and by a surface area of ~270 $m^2/g$. It is thermally stable for most hydrotreating applications such as hydrocracking. However, under hydrothermal conditions, structural stability is significantly reduced and the commercial use of these materials in fluidized cracking applications must be questioned.

In a typical commercial cracking unit like the one represented in Figure 1, steam stripping of occluded hydrocarbons from the catalyst surface is performed at temperatures in the 480–540 °C range. Higher temperatures are seen by the catalyst in the regenerator (600–700 °C) where, however, steam rarely exceeds the 15 wt % limit. The severity of the hydrothermal treatment like the one described in a preceding section is necessary to reduce the structural and catalytic properties of certain fresh commercial catalysts to equilibrium levels in a short (~10 h) period of time. Since different catalysts may deactivate differently, a variety of deactivation conditions are needed to predict the activity of each catalyst in the field (Magee and Blazek, 1976). Because interlayered clays have not been field tested, the appropriate steam deactivation procedure for these materials has not yet been defined.

Interlayered clays can mimic the sorptive as well as some of the catalytic properties of zeolites. Their high cracking activity is believed to be associated with the nature of the pillars used to expand the clay structure. Infrared spectra

zeolite-type cracking. In the pillared Ca-bentonite, the decrease of $C_3^=$ and $C_4^=$ at conversion levels above 70% could be indicative of secondary reactions leading to the formation of high molecular weight hydrocarbons and coke. In the commercial catalysts considered, $C_3^=$ yields mono-

obtained by evacuating pyridine-loaded wafers of a sample of pillared Na-bentonite revealed that the interlayered clay contained both Lewis and Bronsted acid sites and that at 400 °C, under vacuum, surface acidity was mostly of the Lewis type (Occelli and Tindwa, 1982). Similar results were obtained with the pillared Ca-bentonite under study (Occelli and Lester, 1983). The clay Lewis acid sites are believed to be responsible for carbonium ion generation and initiate the mechanism of hydrocarbon cracking.

The fluid catalytic cracking of gas oils and the zeolite-based cracking catalysts used have been reviewed in detail by Venuto and Habib (1979) and by Magee and Blazek (1976). It is generally agreed that the main cracking reaction is the $\beta$-scission of a carbonium ion to form an olefin and a new, lower molecular weight carbonium ion. In the case of a paraffin

$$C_nH_{2n+2} \rightarrow C_nH^+_{2n+1} + H^-$$

$$C_nH^+_{2n+1} \xrightarrow{K_\beta} C_3H_6 + C_{n-3}H^+_{2n-5}$$
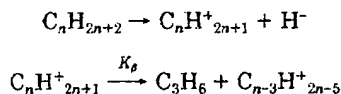
The same carbonium ion can undergo other monomolecular reactions like skeletal isomerization or proton elimination with olefin formation. A reaction with a neutral molecule can result in hydride transfer and the formation of a new carbonium ion

$$C_nH^+_{2n+1} + C_mH_{2m+2} \xrightarrow{K_H} C_nH_{2n+2} + C_mH^+_{2m+1}$$
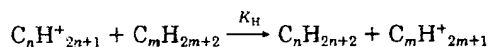
Since hydrogen transfer is bimolecular and $\beta$-scission is monomolecular, the ratio of the two reaction rates will be equal to $(K_H/K_\beta)[C_mH_{2m+2}]$, indicating that hydrogen transfer reactions will be favored by high hydrocarbon concentration at the catalyst surface (Bolton and Lanewala, 1970; Venuto, 1971; Poutsma and Schaffer, 1973). This condition is believed to exist in an interlayered clay since its microspace is easily accessible to $C_5$-$C_{10}$ n-paraffins (Occelli et al., 1982) and branched aromatics such as 1,3,5-trimethylbenzene (Vaughan and Lussier, 1979). Furthermore, equilibrium loadings expressed in mL/g typically represent 60 to 70% of the pore volume of the clay. As in zeolites, the isosteric heat of sorption depends on the sorbate molecular weight and increases from 7.5 kcal/mol for n-pentane to 14.2 kcal/mol for n-decane. The heats of sorption for these paraffins do not deviate greatly from the corresponding heat of condensation, indicating weak sorbate–sorbent interactions (Occelli et al., 1981). Since acidity in the micropore structure is mostly of the Lewis type, hydride abstraction with the formation of carbonium ions is a reasonable possibility. Thus, the cracking of hydrocarbons is terminated at high molecular weight by hydrogen transfer of hydride to these carbonium ions explaining the low slurry oil and high LCGO yields shown in Figures 9 and 10. The lower gasoline make shown in Figure 8 could be caused by iron catalyzed dehydrogenation reactions which produce light gases and coke (see Figures 14–16). Lussier et al. (1980) have shown that by reducing the $Fe_2O_3$ content of the clay from 3.0 to 0.6%, the gasoline/conversion ratio increased from 0.72 to 0.85. Furthermore, it is possible that the hydrogen transfer reactions that prevent secondary cracking of $C_5$-$C_{10}$ hydrocarbons are also responsible for transforming olefins into aromatics (Van Hook and Emmett, 1963) with subsequent coke formation

$$3C_nH_{2n} + C_mH_{2m} = 3C_nH_{2n+2} + C_mH_{2m-6}$$

$$4C_nH_{2n} = 3C_nH_{2n+2} + C_nH_{2n-6}$$

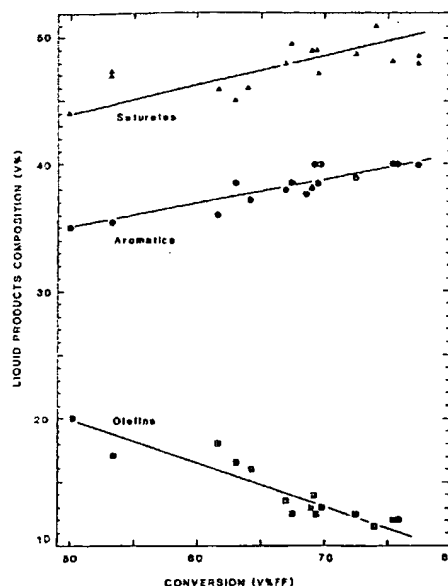$$3C_mH_{2m-2} = 2C_mH_{2m} + C_mH_{2m-6}$$
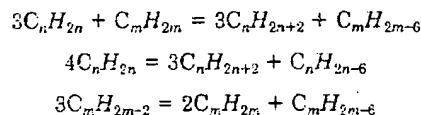


**Figure 17.** Activity effects on liquid products composition.

Olefin yields in the liquid products monotonically decrease with conversion while saturates and aromatics increase (see Figure 17). Aromatics are important coke precursors (Welsh and Rollman, 1977) possibly because of selective sorption on Lewis acid sites since, as reported by Hall et al. (1963), the rate of coke formation is faster on these sites than on Bronsted acid sites. The decrease in olefin yields ($C_3^=$ and $C_4^=$) for conversions above $\sim70\%$ could be indicative of hydrogen redistribution reactions like the ones occurring in polymerization, dehydrocyclization, and aromatization processes which could lead to coke formation. Shepard et al. (1963) have discussed the polymerization of propylene over a silica–alumina catalyst. Van Hook and Emmett (1962) and Hightower and Emmett (1965) have reported that during cracking of $C_{16}H_{34}$, propylene participates in the formation of aromatics and saturates. More recently, the conversion of low molecular weight olefins to hydrocarbons in the gasoline range has been reported by Van den Berg (1980), Garwood and Lee (1980), and Dessau (1980), using ZSM-5 type zeolites. Vedrine et al. (1980) have studied the conversion of ethylene, propene, and butene to aromatics over ZSM-5. Because of the zeolite shape selectivity, the formation of aromatics by conjunct polymerization of olefins occurs with little coke formation. The opposite is probably true in interlayered clays.

### Summary

The pillaring of calcium bentonite with aluminum oligomers generates a microporous structure thermally stable for most fixed-bed applications such as hydrocracking. Under hydrothermal conditions ($\sim95\%$ steam), stability is limited to $\sim620$ °C. The interlayered clay at cracking temperature under vacuum behaves like a strong Lewis acid. After a mild hydrothermal deactivation with 95% steam, the interlayered clay was found to be as active as certain commercial fluid cracking catalysts and showed a greater LCGO selectivity and greater carbon, hydrogen and light gas make.

### Acknowledgment

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# Development of a Low Cost, Thermally Stable, Monolithic Three-Way Catalyst System

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A new three-way catalyst (TWC) system consisting of a palladium (Pd) catalyst as the inlet half and a standard platinum (Pt) and rhodium (Rh) TWC as the outlet half has been investigated. This Pd/TWC system offers improved thermal resistance, light-off performance, and reduction in precious metal cost compared to an equal volume standard TWC. However, several open issues, such as the cost of manufacturing a two-part catalyst system, the poison resistance, and vehicle durability, remain to be resolved. The study of the Pd/TWC system was based on the concept that the activity of the outlet portion of a catalyst can be protected from thermal damage by the inlet portion as long as the inlet remains active. To prove this, a series of catalyst systems with different formulations for the inlet and outlet halves was studied using engine dynamometers. The performances of these catalyst systems were evaluated and compared during and after an emission durability cycle, with and without the imposition of 60 1-min long, 2000 °F episodes with excess air to simulate severe thermal environments experienced in some vehicles. Detailed results will be discussed.

## Introduction

As a part of the effort to reduce automotive emissions, three-way catalysts (TWCs) were developed to simultaneously convert three major pollutants, hydrocarbons (HC), carbon monoxide (CO), and nitrogen oxides ($NO_x$) (Jones et al., 1971; Gandhi et al., 1976; Mooney et al., 1977). Vehicles equipped with TWCs have been shown to meet emission standards with minimal loss of fuel economy and driveability (Seiter and Clark, 1978; Engh and Wallman, 1977; Oser, 1979). Today, TWCs followed by conventional oxidation catalysts (COCs) are used in most U.S. light-duty passenger cars, and their use is expected to continue for some time.

Because of their wide-spread application, improvements in TWCs would be desirable. Most TWCs contain platinum (Pt) and rhodium (Rh) as active metal components. These precious metals (PMs) are imported and expensive. In addition, Pt is susceptible to sintering at high temperature (Yao et al., 1980), and the minute amount of Rh in TWCs is known to interact with the alumina ($Al_2O_3$) washcoat at temperatures above 1650 °F under lean air-fuel ratio (A/F) conditions to form a catalytically inactive spinel (Yao et al., 1977). Therefore, in order to maintain good TWC activity after high temperature exposure, the conventional method is to increase the PM loading on TWCs. As a result, the cost of TWCs can be high.

**KIRK-OTHMER**

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# CARBON BLACK

Carbon black is a generic term for an important family of products used principally for the reinforcement of rubber, as a black pigment, and for its electrically conductive properties. It is a fluffy powder of extreme fineness and high surface area, composed essentially of elemental carbon. Plants for the manufacture of carbon black are strategically located worldwide in order to supply the rubber tire industry, which consumes 70% of production. About 20% is used for other rubber products and 10% is used for special nonrubber applications. World capacity in 1988 was estimated at over six million metric tons; U.S. capacity was almost 1.6 million metric tons. Carbon black was ranked 38 in 1989 among the 50 largest volume industrial chemicals produced in the United States. Six U.S. manufacturers (1) were operating 22 plants in 1990. Many of these are located in the south and southwest. Over 35 grades, listed in ASTM 1765-87 (2), are used by the rubber industry, and one manufacturer supplies an additional 45 grades for special pigment applications.

Carbon blacks differ from other forms of bulk carbon such as diamond, graphite, cokes, and charcoal in that they are particulate, composed of aggregates having complex configurations, quasigraphitic in structure, and of colloidal dimensions. They differ from other bulk carbons in having their origin in the vapor phase through the thermal decomposition and the partial combustion of hydrocarbons. Carbon black is a product of a process incorporating the latest engineering technology and process controls. Its purity differentiates it from soots that are impure by-products from the combustion of coal and oils and from the use of diesel fuels. Carbon blacks are essentially free of the inorganic contaminants and extractable organic residues characteristic of most forms of soot.

A number of processes have been used to produce carbon black including the oil-furnace, impingement (channel), lampblack, and the thermal decomposition of natural gas and acetylene (3). These processes produce different grades of carbon

and are referred to by the process by which they are made, eg, oil-furnace black, lampblack, thermal black, acetylene black, and channel-type impingement black. A small amount of by-product carbon from the manufacture of synthesis gas from liquid hydrocarbons has found applications in electrically conductive compositions. The different grades from the various processes have certain unique characteristics, but it is now possible to produce reasonable approximations of most of these grades by the oil-furnace process. Since over 95% of the total output of carbon black is produced by the oil-furnace process, this article emphasizes this process.

### History of Carbon Black Manufacture

The use of carbon black as a pigment dates back to prehistoric times. Cave wall dwellings and objects from ancient Egypt were decorated with paints and lacquers containing carbon black. The oldest process practiced in China about 3000 BC consisted of the partial combustion of vegetable oils in small lamps with ceramic covers. The smoke impinged on the covers from which the adhering carbon black was carefully removed. Another old process is the lampblack process, which is the ancestor of all modern carbon blacks. Until the 1870s it was the only commercial process, and because of this the word lampblack is occasionally used as a generic term for carbon black. In the lampblack process, oils are burned in open, shallow pans in a restricted air supply. The heavy, carbon-laden smoke is passed through a series of settling chambers and filters from which the flocculated carbon deposits are recovered.

Prior to 1870 it was already known that carbon black with much higher covering power and jetness could be recovered from underventilated illuminating gas flames impinging on a cold surface. These gas blacks led to the development of the channel process, the name deriving from the iron channels used for the collection of the carbon blacks from the impingement of thousands of small luminous flames burning in a restricted atmosphere of air. This process dominated the industry for over 50 years. In 1926 there were 33 producers in the United States. Because of poor carbon yields from natural gas in the range of 1–5% and severe atmospheric pollution, this process has become extinct. The last channel black plant in the United States was closed in 1976.

In the 1920s two other processes using natural gas were introduced that gave much higher yields with large decreases in atmospheric contamination. One was the cyclic thermal black process. Alternate heating and production cycles in large brick checkered chambers are used to produce a unique large particle size, essentially unaggregated-grade useful for many special rubber and plastic applications. Thermal black is produced in the United States, Canada, England, and a few other locations worldwide. The other process, based on natural gas, was the so-called gas-furnace process and is no longer used. This process was continuous and the forerunner of the oil-furnace process. It was discontinued because of the relatively low yield, high raw material cost, and limited range of products.

The first commercial oil-furnace process was put into operation in 1943 by the Phillips Petroleum Co. in Borger, Texas. The oil-furnace blacks rapidly displaced all other types used for the reinforcement of rubber and today account

for practically all carbon black production. In the oil-furnace process heavy aromatic residual oils are atomized into a primary combustion flame where the excess oxygen in the primary zone burns a portion of the residual oil to maintain flame temperatures, and the remaining oil is thermally decomposed into carbon and hydrogen. Yields in this process are in the range of 35 to 50% based on the total carbon input. A broad range of product qualities can be produced.

Before World War I carbon black was almost exclusively used as a black pigment for printing inks, paints, and enamels. The singular event that changed the industry from a small specialty product manufacturer to large volume producer of a vital raw material was the discovery of rubber reinforcement in 1904 (4). The automobile and the tire industries were expanding rapidly, and there was a demand for longer wearing automobile tires. The use of carbon black as a filler for rubber fulfilled this need providing longer wearing and more durable pneumatic tires. The use of carbon black in tires remains its most important application, coupling the fortunes of the carbon black industry to that of the automotive industry.

## Physical Structure of Carbon Black

**Molecular and Crystallite Structure.** The arrangement of carbon atoms in carbon black has been well-established by x-ray diffraction methods (5,6). The diffraction patterns show diffuse rings at the same positions as diffraction rings from pure graphite. The suggested relation to graphite is further emphasized as carbon black is heated to 3000°C. The diffuse reflections sharpen, but the pattern never achieves that of true graphite. Carbon black can have a degenerated graphitic crystallite structure. Whereas graphite has three-dimensional order, as seen in the model structures of Figure 1, carbon black has two-dimensional order. The x-ray data indicate that carbon black consists of well-developed graphite platelets stacked roughly parallel to one another but random in orientation with respect to adjacent layers. As shown in Figure 1 the carbon atoms in the graphite structure form large sheets of condensed aromatic ring systems with an inter-atomic spacing of 0.142 nm, comparable to the aromatic carbon separation distance of 0.139 nm in benzene. The large graphite interplanar distance of 0.335 nm results in a specific gravity of 2.26. In carbon black the interplanar distance is still larger, in the range of 0.350–0.365 nm, as a consequence of the random planar orientations or so-called turbostratic arrangement. The specific gravities of commercial carbon blacks are 1.76–1.90 depending on the grade. X-ray diffraction data provide estimates of crystallite size. $L_a$ is the average layer plane diameter and $L_c$ is the average crystallite thickness. For a typical carbon black $L_a$ is 1.7 nm and $L_c$ is 1.5 nm, which corresponds to an average of four layer planes per crystallite containing 375 carbon atoms. A particle of a 100 m²/g carbon black contains over 4000 crystallites. It was originally suggested that these discrete crystallites were in random orientation within the particle. This view was later abandoned when electron microscopy of graphitized and oxidized carbon blacks indicated more of a concentric layer plane arrangement. This structure has been confirmed by the use of high resolution phase-contrast electron microscopy that made possible the direct imaging of graphitic layer planes in carbon black (7).

Figure 2 shows a phase-contrast electron micrograph of carbon black at high resolution that displays the marked concentric arrangement of the layer planes at the surface and around what appear to be growth centers.
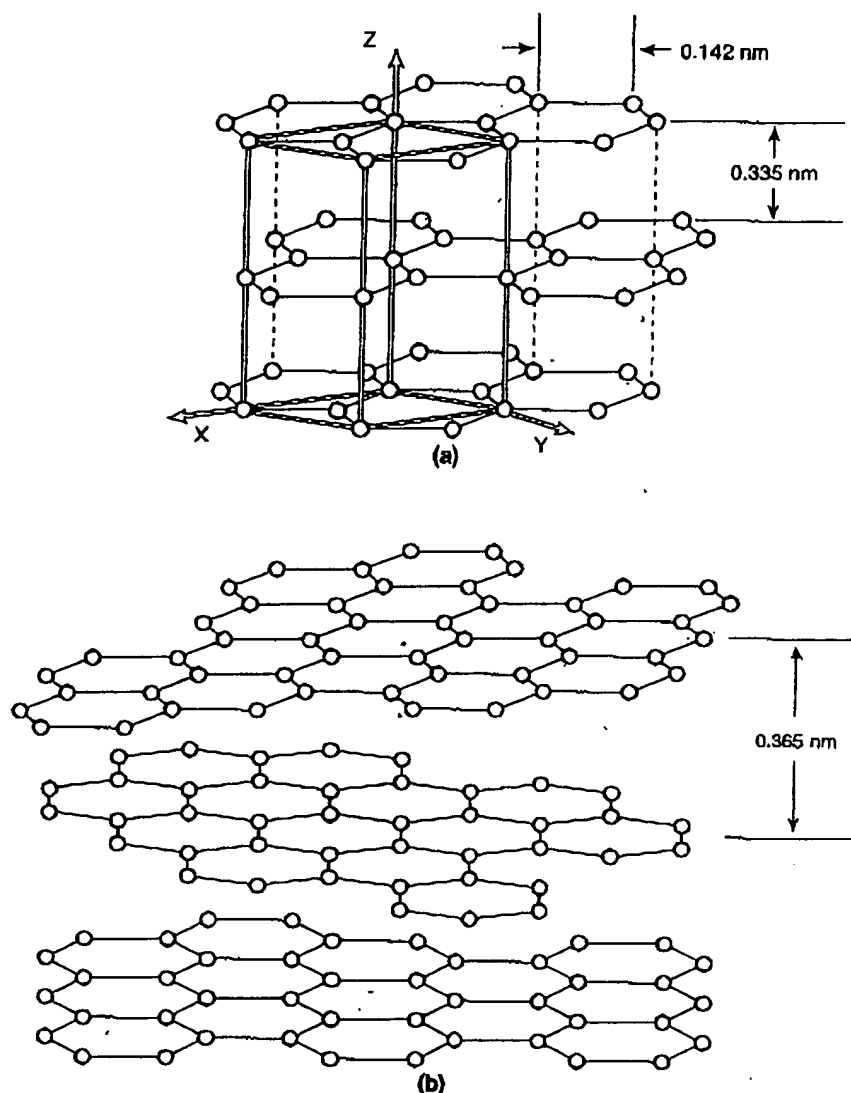


**Fig. 1.**   Atomic structural models of (a), graphite, and (b), carbon black.

The word particle has become so widely used in the technical rubber and carbon black literature that it is convenient to retain the term when in fact nodule is meant. The layer planes are curved, distorted, and of varying size. They also intersect and interconnect one particle or nodule with its neighbors. This type of structure has been termed paracrystalline. It is obvious that individual particles do not exist in carbon blacks, with the exception of thermal blacks, and that the functional unit is an aggregate of nodules that probably existed as smaller particles at some early stage of the carbon formation process. The functional unit in well-dispersed systems is called an aggregate.
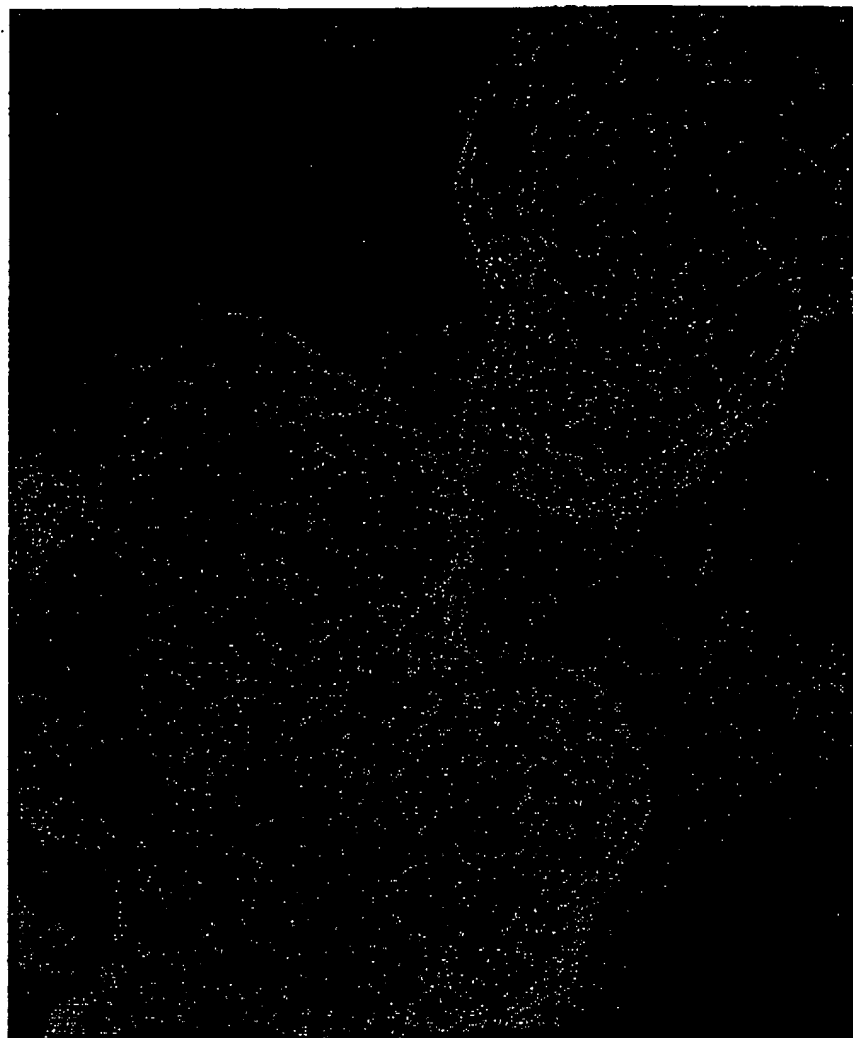
**Fig. 2.** High resolution (3,000,000 ×) electron micrograph of H-300-grade carbon black. Courtesy of W. M. Hess.

**Morphology.** In describing carbon black, three terms are used to describe structures of increasing scale and complexity:

*Particles* (nodules) are the primary structure element. They are roughly spherical elements that are joined in the aggregate structures.

*Aggregates* are the primary dispersable elements of carbon black in all but thermal blacks. The particles in an aggregate are connected and have grown together.

*Agglomerates* are undispersed clusters of aggregates held together by van der Waals forces or by binders. The term structure is used to describe both the extent and the complexity with which the particles are interconnected in aggregates. Primary measures of structure focus on the internal space within the aggregate.

Size and shape of the aggregates in composite systems are the principal features that determine the performance of carbon black as a reinforcing agent and as a pigment (8). Figure 3 shows an electron micrograph of a reinforcing tread black. There is an enormous range in aggregate size. The aggregate size distribution curve for N220 shown in Figure 4 is log-normal, and the range of $D_c$, equivalent diameters of the projected areas of the aggregates is about-tenfold. Within each aggregate the nodules, or particles, appear to be about the same size. The size of the aggregates is directly related to the size of the particles. The shapes of the aggregates have infinite variety from tight grapelike clusters to open dendritic or branched arrangements to fibrous configurations.
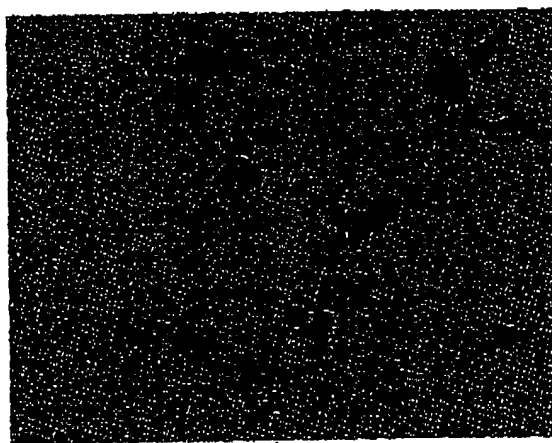
**Fig. 3.**  Electron micrograph of reinforcing-grade of N399 tread black (100,000 ×).

**Fig. 4.**  Aggregate size distributions by electron microscope image analysis ($D_e$) and centrifugal ($\bar{D}_{St}$) sedimentations for N220 and N351 carbon blacks (8).

A useful method for determining relative aggregate sizes and distributions is by centrifugal sedimentation. From the sedimentation rates of the aggregates the Stokes diameter is derived. A convenient instrument for these measurements is the Joyce Loebl disk photosedimentometer (9). Large aggregates sediment at a faster rate than smaller ones. The sedimentation rate is also influence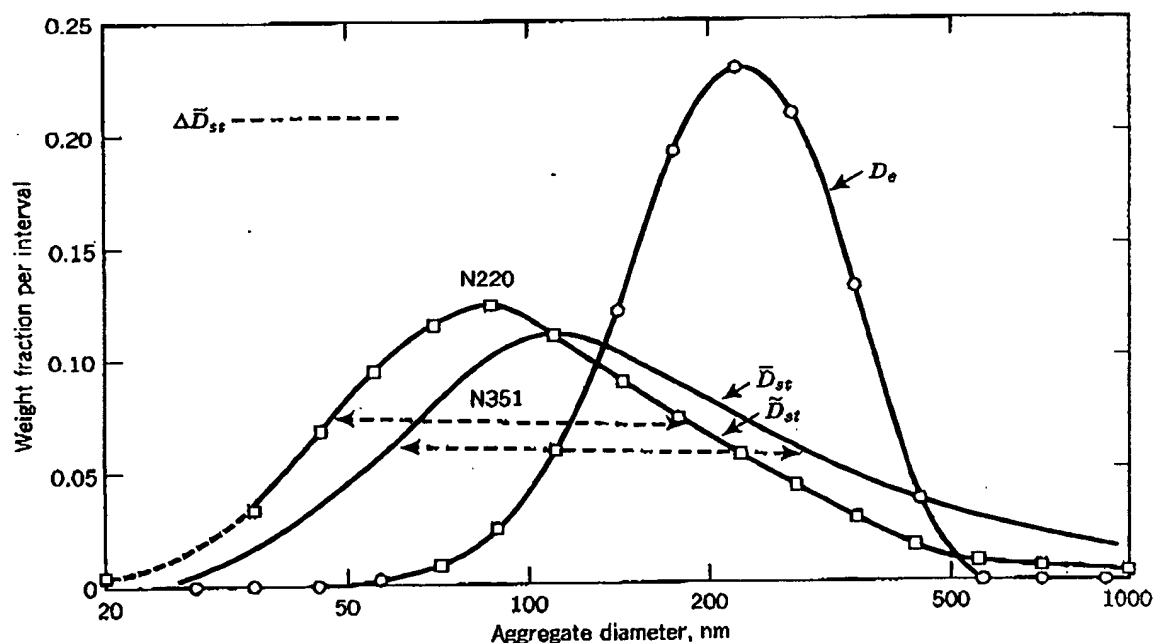d by the bulkiness of the aggregates. At constant volume or mass, a bulky aggregate sediments more slowly than a compact aggregate because of frictional drag. Figure 4 (8) shows a comparison of a Stokes diameter distribution $\tilde{D}_{St}$ and equivalent diameter distribution $D_e$ from electron microscopy for N220. In this example the modal $\tilde{D}_{St}$ value is about one-third of the modal $D_e$ value.

Table 1 lists average $\tilde{D}_{St}$ values from a number of literature sources. This table also lists $d_{wm}$ values for the aggregates calculated from their estimated volumes. In this case there is reasonable agreement between the two diameters. Aggregate size distributions from centrifugal sedimentation analysis are very useful for assessing the differences in this characteristic within a given grade or at constant surface area. It has been shown that the hysteresis of rubber vulcanizates can be reduced by broadening the aggregate size distribution curve without any significant loss in abrasion resistance (11,12). As shown in Figure 4 this broadening is usually expressed as $\Delta D_{50}$, the width at 50% of the modal value. $\tilde{D}_{St}$ values have been related to the dynamic and mechanical performance of rubber-grade carbon blacks. Hysteresis decreases and abrasion loss increases with increasing values of $\tilde{D}_{St}$ (13).

**Table 1. Carbon Black Morphology[a]**

| ASTM designation | Particle size, $d_{wm}$[b], nm | Aggregate size, $d_{wm}$[b], nm | $\tilde{D}_{St}$[c], nm | Surface area, $m^2/g$ |
|---|---|---|---|---|
| N110 | 27 | 93 | 76–111 | 143 |
| N220 | 32 | 103 | 95–117 | 117 |
| N234 | 31 | 109 | 74–97 | 120 |
| N326 | 41 | 108 | 98 | 94 |
| N330 | 46 | 146 | 116–145 | 80 |
| N339 | 39 | 122 | 96–125 | 96 |
| N351 | 50 | 159 | 127 | 75 |
| N375 | 36 | 106 | 91 | 105 |
| N550 | 93 | 240 | 220–242 | 41 |
| N660 | 109 | 252 | 227–283 | 34 |
| N774 | 124 | 265 | 261 | 30 |
| N990 | 403 | 593 | 436 | 9 |

[a]Ref. 10. Particle size, aggregate size, and surface area are by em.

[b]$d_{wm}$ = weight mean diameter = $\dfrac{nd^4}{nd^3}$.

[c]Stokes diameter by centrifugal sedimentation from various sources.

The tinting strength of rubber-grade carbon blacks shows a linear relationship with $\tilde{D}_{St}$ shown in Figure 5. Since performance characteristics are known to

depend on aggregate volume, surface area, and bulkiness, it appears that the $\tilde{D}_{St}$ values combine the effects of all these factors. As such, it is a valuable addition to carbon black characterization methodology.
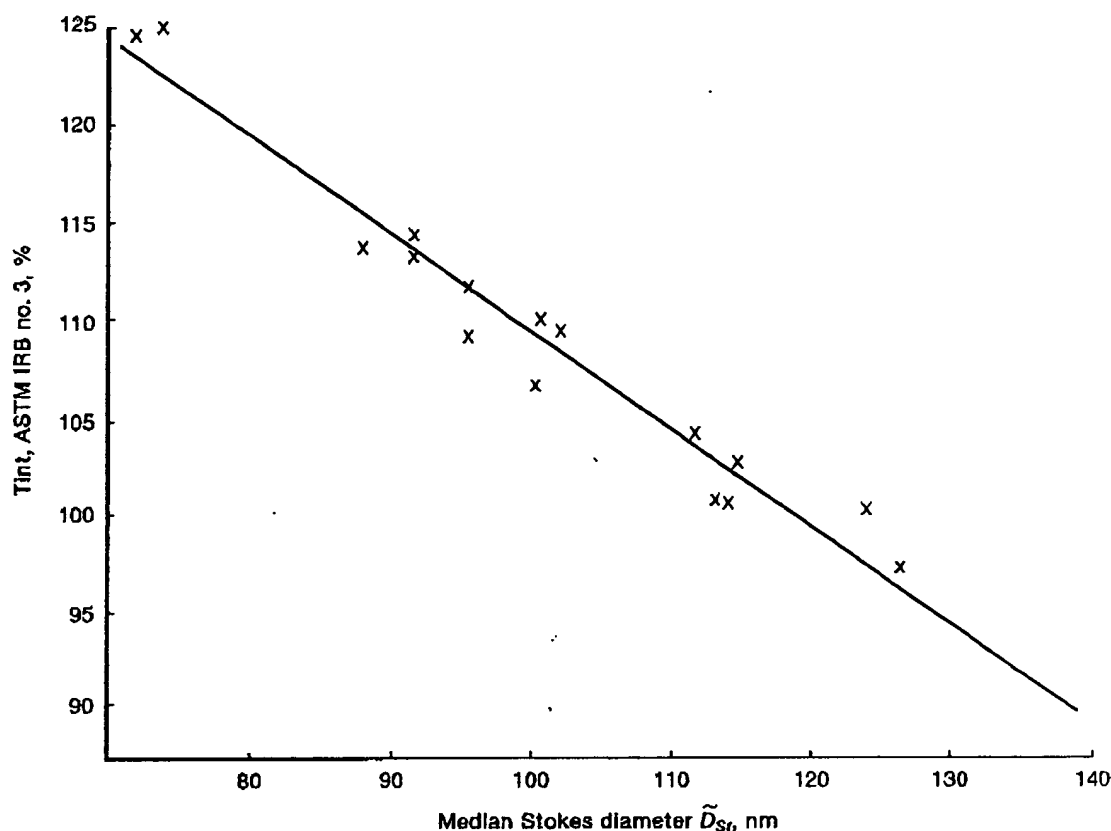


**Fig. 5.**   Tinting strength versus median Stokes diameters for a range of reinforcing tread blacks.

**Aggregate Morphology and Structure.**   The term structure is widely used in the carbon black and rubber industries. It was originally introduced in 1944 (14) to describe a chaining tendency of the carbon black particles. It is now used to describe the relative void volume characteristics of grades of black of the same surface area. Structure comparisons of grades with different surface areas cannot be made. It is now known that the properties associated with structure are associated principally with the bulkiness of individual aggregates. Aggregates of the same volume, surface area, and number of nodules have high structure in the open bulky and filamentous arrangement and a low structure in a more clustered compact arrangement.

High structure blacks in unvulcanized rubber give higher Mooney viscosities, lower die swell, faster extrusion rates, and better and more rapid dispersion after incorporation. In vulcanized rubber higher modulus is obtained. High structure blacks give lower bulk densities and high vehicle demand in paint systems.

Structure is usually measured by a void volume test such as the absorption

of dibutyl phthalate (DBPA) (15), or by bulk density measurements of the carbon black under compression. In order to eliminate the effects of pelletizing conditions the DBPA test has been modified to use a sample that has been precompressed at a pressure of 165 MPa (24,000 psi) and then broken up four successive times (24M4) (16). This procedure causes some aggregate breakdown and is claimed to more closely approximate the actual breakdown that occurs during rubber mixing.

**Aggregate Breakdown.** Aggregate size analysis by the electron microscope and centrifuge methods are performed on predispersed samples of carbon black. High shear energy, usually ultrasonic, and enough time are employed in these sample preparations to break down microagglomerates to their ultimate aggregates for measurement. When mixed into elastomers under high shear conditions the aggregates themselves undergo fracture forming smaller aggregates that become the actual functional units (17–19). The extent of breakdown depends on shearing stress, energy input, and the grade of carbon black. Elastomer mixes were studied using the techniques of ultramicrotome and automated image analysis. Ultrasonic dispersions of carbon gel preparations from elastomer mixes have also been used in breakdown studies. A high DBPA reinforcing tread grade (N347) exhibited a significant reduction in aggregate length in a BR/OEP tread formulation, whereas a low DBPA grade (N326) showed no measurable change. The extent of aggregate length reduction was 30 to 40% for the normal and high DBPA grades (20).

The effect of elastomer viscosity on aggregate breakdown has been shown (19). A high DBPA grade (N339) was well-mixed with a 52 and a 100 Mooney viscosity OE-SBR. A 43% reduction in aggregate volume was reported for the 52 Mooney rubber and a 53% reduction for 100 Mooney rubber. High resolution electron micrographs show actual fracture locations at the ends of aggregates. The extent of fracture from aggregate length and volume breakdown is consistent with one average fracture per aggregate for the high DBPA grades.

## Chemical Composition

Oil-furnace blacks used by the rubber industry contain over 97% elemental carbon. Thermal and acetylene black consist of over 99% carbon. The ultimate analysis of rubber-grade blacks is shown in Table 2. The elements other than carbon in furnace black are hydrogen, oxygen, and sulfur, and there are mineral oxides and salts and traces of adsorbed hydrocarbons. The oxygen content is located on the surface of the aggregates as $C_xO_y$ complexes. The hydrogen and sulfur are distributed on the surface and the interior of the aggregates. Some special blacks used for pigment purposes contain larger quantities of oxygen than normal furnace blacks. These blacks are made by oxidation in a separate process step using nitric acid, ozone, air, and other oxidizing agents. They may contain from 2 to 6% oxygen. Oxidation improves dispersion and flow characteristics in pigment vehicle systems such as lithographic inks, paints, and enamels. In rubber-grade blacks surface oxidation reduces pH and changes the kinetics of vulcanization, making the rubber compounds less scorchy and slower curing.

**Table 2. Chemical Composition of Carbon Blacks, %**

| Type | Carbon | Hydrogen | Oxygen | Sulfur | Ash | Volatile |
|---|---|---|---|---|---|---|
| rubber-grade furnace | 97.3–99.3 | 0.20–0.40 | 0.20–1.20 | 0.20–1.20 | 0.10–1.00 | 0.60–1.50 |
| medium thermal | 99.4 | 0.30–0.50 | 0.00–0.12 | 0.00–0.25 | 0.20–0.38 | |
| acetylene | 99.8 | 0.05–0.10 | 0.10–0.15 | 0.02–0.05 | 0.00 | <0.40 |

A convenient method for assessing the extent of surface oxidation is the measurement of volatile content. This standard method measures the weight loss of the evolved gases on heating up to 950°C in an inert atmosphere. The composition of these gases consists of three principal components: hydrogen, carbon monoxide, and carbon dioxide. The volatile content of normal furnace blacks is under 1.5%, and the volatile content of oxidized special grades is 2.0 to 9.5%.

The origin of the volatile gases is the functional groups attached to the carbon black layer planes. These groups are carbon-bound hydrogen, phenols, hydroquinones, quinones, neutral groups with one oxygen, carboxylic acids, lactones, and neutral groups containing two oxygens (21). Hydrogen is the most dominant of these groups. The oxygen content is present mainly as weakly acidic phenolic groups located at the surface of the aggregates. Figure 6 shows an idealized graphite surface layer plane with the various functional groups located at the periphery of the plane.
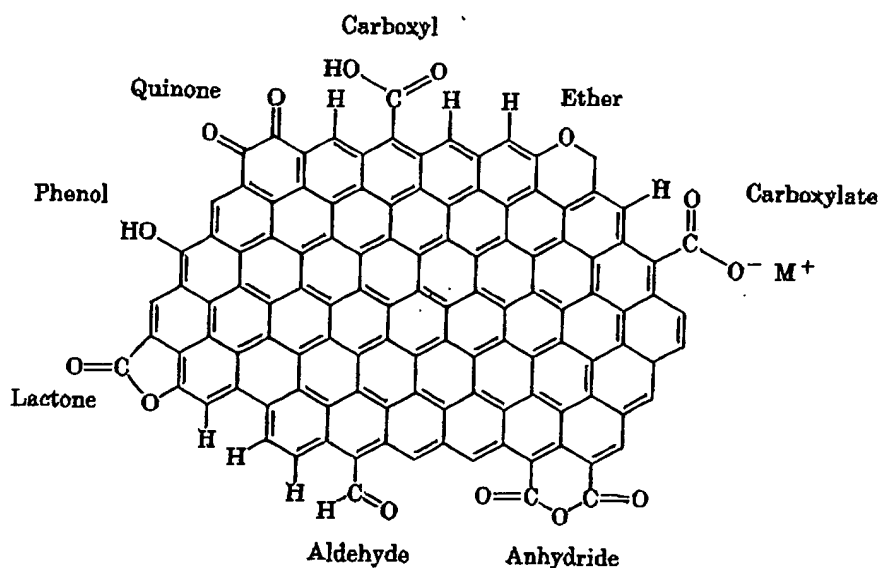


**Fig. 6.** Aromatic layer plane with functional side groups.

In addition to combined hydrogen and oxygen, carbon blacks may contain as much as 1.2% combined sulfur resulting from the sulfur content of the aromatic feedstock that contains thiophenes, mercaptans, and sulfides. The combined sulfur appears to be inert and does not contribute to sulfur cross-linking during the vulcanization of rubber compounds.

The ash content of furnace blacks is normally a few tenths of a percent but in some products may be as high as one percent. The chief sources of ash are the water used to quench the hot black from the reactors during manufacture and for wet pelletizing the black. The hardness of the water, and the amount used determines the ash content of the products. The ash consists principally of the salts and oxides of calcium, magnesium, and sodium and accounts for the basic pH (8–10) commonly found in furnace blacks. In some products potassium, in small amounts, is present in the ash content. Potassium salts are used in most carbon black manufacture to control structure and rubber vulcanizate modulus (22). The basic mineral salts and oxides have a slight accelerating effect on the vulcanization reaction in rubber.

## Carbon Black Formation Mechanisms

The formation of carbon black in a candle flame was the subject of a series of lectures in the 1860s by Michael Faraday at the Royal Institution in London (23). Faraday described the nature of the diffusion flame, the products of combustion, the decomposition of the paraffin wax to form hydrogen and carbon, the luminosity of the flame because of incandescent carbon particles, and the destructive oxidation of the carbon by the air surrounding the flame. Since Faraday's time, many theories have been proposed to account for carbon formation in a diffusion flame, but controversy still exists regarding the mechanism (24).

Mechanisms of formation must account for the unique morphology and microstructure of carbon black. These features include the presence of nodules, or particles, multiple growth centers within some nodules, the fusion of nodules into large aggregates, and the paracrystalline or concentric layer plane structure of the aggregates. One mechanism of formation involves the decomposition of the aromatic hydrocarbon fuel in a diffusion flame to hydrogen and carbon radicals, and carbon–hydrogen radical fragments. These combine into larger aromatic layer plane units until they are no longer stable and condense out of the vapor phase to form nuclei, or growth centers. Further carbon deposition forms carbon particles that are the precursors of the nodules. The carbon particles collide and coalesce while undergoing further deposition of carbon layer planes and their surface, forming the nodules and aggregates with their characteristic onion microstructure as seen in the micrographs (25). The various steps in the sequence are not well understood. There is particular disagreement regarding the nucleation and particle formation steps preceding the formation of nodules. One suggestion is that the particles go through a fairly sticky stage as they collide and coalesce to form the aggregates. Another suggestion is that the layer planes formed in the vapor phase condense out to form solid multiple layer plane nuclei. Carbon deposition on the nuclei results in particles and eventually nodules and aggregates. The remarkable and industrially important influence of ionic species such as $K^+$ and $Ca^{2+}$ on the morphology of the aggregates and their surface area during the carbon black formation process is a strong indication that ionic mechanisms may be active in the nucleation and aggregate formation steps (22). There are several reviews of carbon formation mechanisms (26,27).

## Manufacture

### THE OIL-FURNACE PROCESS

The oil-furnace process, based on the partial combustion of liquid aromatic residual hydrocarbons, was first introduced in the United States at the end of World War II. It rapidly displaced the then dominant channel (impingement) and gas-furnace processes because it gave improved yields and better product qualities. It was also independent of the geographical source of raw materials, a limitation on the channel process and other processes dependent on natural gas, making possible the worldwide location of manufacturing closer to the tire customers. Environmentally it favored elimination of particulate air pollution and was more versatile than all other competing processes.

A simplified flow diagram of a modern furnace black production line is shown in Figure 7 (28). The principal pieces of equipment are the air blower, process air and oil preheaters, reactors, quench tower, bag filter, pelletizer, and rotary dryer. The basic process consists of atomizing the feedstock into the combustion zone of the reactor where the combustion of natural gas and preheated excess air create a high temperature environment of 1200 to 1900°C that almost instantly vaporizes the feedstock and decomposes most of it to carbon black and hydrogen. The remaining feedstock reacts with the excess oxygen in the primary combustion stream to maintain the reaction temperature for carbon formation. In some reactors a number of feedstock streams are atomized radially into the high velocity combustion gases. The reaction products must be quenched rapidly with water sprays to lower the temperature to prevent loss of the carbon black product through reaction with carbon dioxide and water, products of the combustion reactions. The hot, heavy carbon black smoke from the reactors enters the air preheater where thermal energy is transferred to preheat the primary combustion air. From the air preheater the lower temperature combustion products are given a secondary quench for a further lowering of temperature in a tower from which they enter the bag filter that separates the fluffy carbon black product from the tail gases. Since the tail gases are composed mainly of water, nitrogen, carbon monoxide, carbon dioxide, and hydrogen, they have heating value as a fuel to supplement the natural gas used to preheat feedstock and for heating the pellet dryers. Unused tail gas is frequently flared prior to venting to the atmosphere after removal of particulate matter. The fluffy carbon black from the bag filter is mechanically agitated to increase its bulk density and is then conveyed to the wet pelletizers where water is added to transform the product into wet granules. Dry pelletization in rotating drums is practiced for some special applications. The wet pellets are then dried in a rotary dryer after which finished product goes to storage tanks for shipping in bulk or in bags.

**Feedstocks.** Feedstocks are viscous aromatic hydrocarbons consisting of branched polynuclear aromatics with smaller quantities of paraffins and unsaturates. Preferred feedstocks are high in aromaticity, free of coke and other gritty materials, and contain low concentrations of asphaltenes, sulfur, and alkali metals. Other limitations are the quantities available on a long-term basis, uniformity, ease of transportation, and cost. The ability to handle such oils in tanks, pumps, transfer lines, and spray nozzles are also primary requirements.
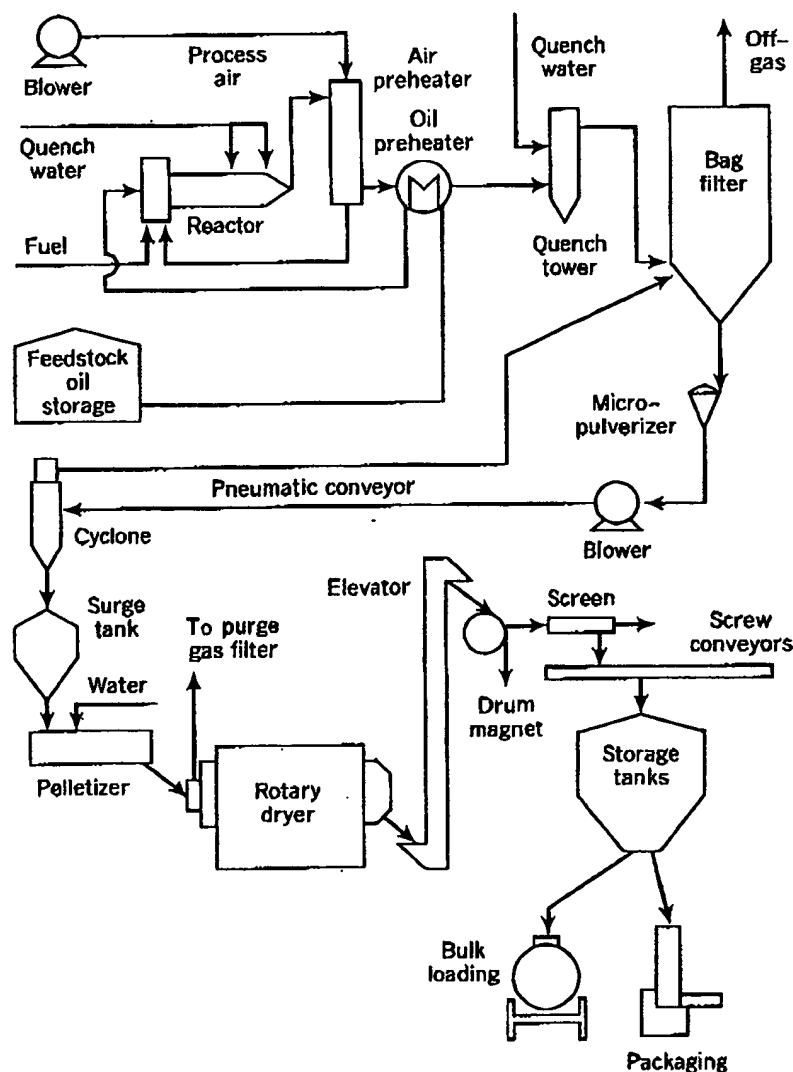
**Fig. 7.  Flow diagram of oil-furnace black process.**

The principal sources of feedstocks in the United States are the decant oils from petroleum refining operations. These are clarified heavy distillates from the catalytic cracking of gas oils. About 95% of U.S. feedstock use is decant oil. Another source of feedstock is ethylene process tars obtained as the heavy by-products from the production of ethylene by steam cracking of alkanes, naphthas, and gas oils. There is a wide use of these feedstocks in European production. European and Asian operations also use significant quantities of coal tars, creosote oils, and anthracene oils, the distillates from the high temperature coking of coal. European feedstock sources are 50% decant oils and 50% ethylene tars and creosote oils.

Aromaticity is the most important property of a carbon black feedstock. It is generally measured by the Bureau of Mines Correlation Index (BMCI) and is an indication of the carbon-to-hydrogen ratio. The sulfur content is limited to reduce corrosion, loss of yield, and sulfur in the product. It may be limited in certain locations for environmental reasons. The boiling range must be low enough so that it will be completely volatilized under furnace time–temperature conditions.

Alkane insolubles or asphaltenes must be kept below critical levels in order to maintain product quality. Excessive asphaltene content results in a loss of reinforcement and poor treadwear in tire applications.

The pricing of carbon black feedstocks depends on their alternate market as residual fuel oil, especially that of high sulfur No. 6 fuel oil. The actual price is determined by the supply/demand relationships for these two markets. Feedstock cost contributes about 60% of the total manufacturing cost. The market price of carbon black is strongly dependent on the feedstock cost as shown in Figure 8.
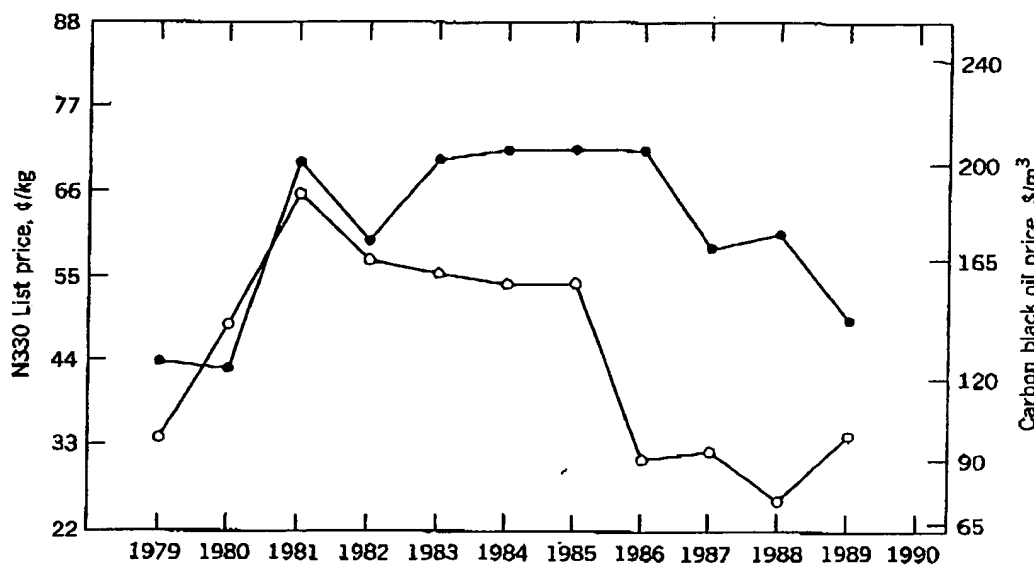


Fig. 8.   Carbon black price and raw material cost in the United States (1979–1989). Average U.S. list price N330 (HAF)-grade carbon black, ¢/kg. To convert $/m$^3$ to $/barrel, multiply by 0.159.

**Reactors.**   The heart of a furnace black plant is the furnace or reactor where carbon black formation takes place under high temperature, partial combustion conditions. The reactors are designed and constructed to be as trouble-free as possible over long periods of operation under extremely aggressive conditions. They are monitored constantly for signs of deterioration in order to ensure constant product quality. The wide variety of furnace black grades for rubber and pigment applications requires different reactor designs and sizes to cover the complete range, though closely related grades can be made in the same reactor by adjusting input variables. Reactors for higher surface area and reinforcing grades operate under high gas velocities, temperatures, and turbulence to ensure rapid mixing of reactant gases and feedstock. Lower surface area and less reinforcing grades are produced in larger reactors at lower temperatures, lower velocities, and longer residence time. Table 3 lists carbon formation temperatures, residence times, and maximum velocities for the complete surface area range of rubber-grade blacks. The N-series designation is in accordance with ASTM D1765, which is the standard classification system for carbon blacks used in rubber products (15). At least three different reactor designs must be used to make this range of furnace blacks and thermal black.

**Table 3. Time—Temperature—Velocity Conditions in Carbon Black Reactors[a]**

| | Surface area, $m^2/g$ | Temperature, °C | Residence time, s | Maximum velocity, m/s |
|---|---|---|---|---|
| N100 series, SAF[b] | 145 | 1800 | 0.008 | |
| N200 series, ISAF[b] | 120 | | 0.010 | 180–400 |
| N300 series, HAF[c] | 80 | 1550 | 0.031 | |
| N500 series, FEF[d] | 42 | | 1.0 | 30–80 |
| N700 series, SRF[e] | 25 | 1400 | 1.5 | 0.5–1.5 |
| N990 thermal | 8 | 1200–1350 | 10 | 10 |

[a]These characteristic conditions and values depend on reactor designs and fuel rates.
[b]SAF = super abrasion furnace; ISAF = intermediate super abrasion furnace.
[c]HAF = high abrasion furnace.
[d]FEF = fast extrusion furnace.
[e]SRF = semireinforcing furnace.

Reactors are built to have three fairly well-defined zones. Gas and air are introduced into an upstream, primary combustion zone. For reinforcing grades, this connects with a mixing zone of high velocity and turbulence where feedstock is introduced as a fine atomized spray. The mixing zone is followed by a reaction zone of cylindrical shape where carbon-forming reactions occur. Downstream of the reaction zone is a water quench. For high surface area blacks the reactors may have a 15 to 38 cm diameter mixing zone with lengths up to five m. For lower area blacks the reactors are cylindrical with diameters of 75 cm or more and lengths of 9 to 12 m. There is a wide variety of reactors, and each manufacturer has proprietary designs. Air and gas may be introduced to the primary combustion zone either axially, tangentially, or radially. The feedstock can be introduced into the primary flame either axially or radially in the high velocity section of the mixing zone. The high velocity section may be venturi-shaped or consist of a narrow diameter choke. The reactors have a steel shell construction lined with high temperature-resistant castable refractories and insulating cements. The refractories have a service life of one to three years. Figures 9 and 10 show the designs of commercial reactors based on the patent literature.

The quality and yield of carbon black depends on the quality of the feed-stock, reactor design, and input variables. The structure is controlled by the addition of alkali metals to the reaction or mixing zones. Usual practice is to use aqueous solutions of alkali metal salts such as potassium chloride or potassium hydroxide sprayed into the combustion chamber or added to the make oil in the oil injector. Alkaline-earth compounds such as calcium acetate that increase the specific surface area are introduced in a similar manner.

The energy utilization in the production of one kilogram of oil-furnace carbon black is in the range of $9.3$–$16 \times 10^7$ J ($4$–$6.9 \times 10^4$ Btu/lb), and the yields are $300$–$660$ kg/$m^3$ ($2.5$–$5.5$ lb/gal) depending on the grade. The energy inputs to the reactor are the heat of combustion of the preheated feedstock, heat of com-bustion of natural gas, and the thermal energy of the preheated air. The energy output consists of the heat of combustion of the carbon black product, the heat of combustion and the sensible heat of the tail gas, the heat loss from the water
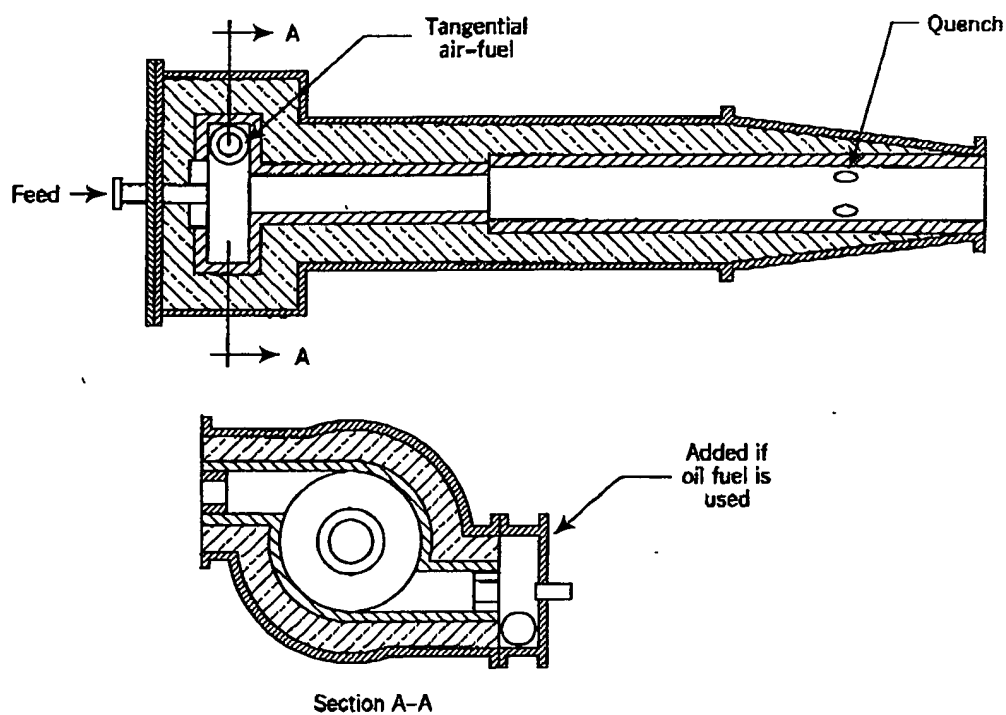
**Fig. 9.   Reactor for HAF-ISAF (N300-N200) carbon blacks. Courtesy of Phillips Petroleum Co.**
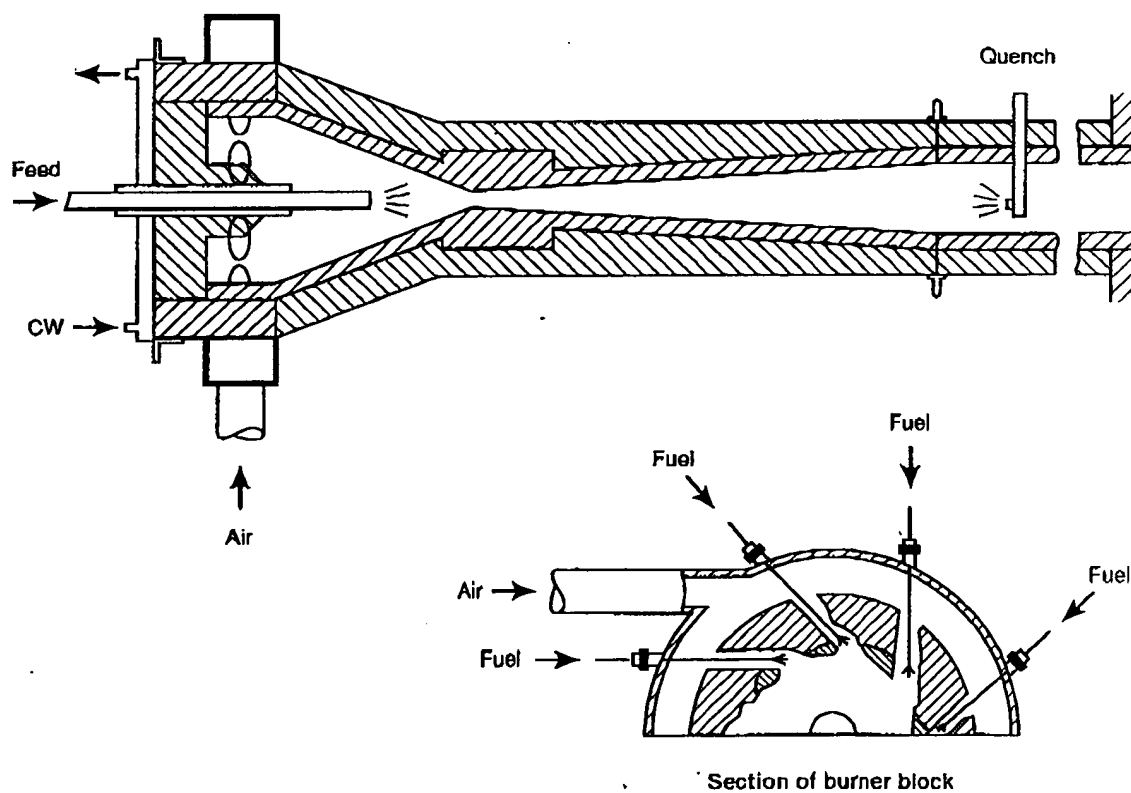
**Fig. 10.   Columbian reactor for tread blacks. CW = cold water.**

quench, heat loss by radiation to atmosphere, and the heat transferred to preheat the primary combustion air. The energy balance for a N300 type of reinforcing grade is shown in Table 4. In this example the thermal efficiency of the process (without tail gas utilization) is 37% for a carbon yield of 0.63 kg/L (5 lb/gal), 61% based on feedstock.

**Table 4.** Energy Balance for Reinforcing Grade of Carbon Black

| *Energy input* | |
| --- | --- |
| energy from feedstock (288°C preheat) | 73% |
| energy from natural gas | 23% |
| air preheat (400°C) | 4% |

| *Energy output* | |
| --- | --- |
| carbon product (heat of combustion) | 37% |
| tail gas (heat of combustion and sensible heat) | 39% |
| heat loss from water quench | 14% |
| heat loss to atmosphere | 6% |
| air preheat (400°C) | 4% |

## THERMAL BLACK PROCESS

Thermal black is a large particle size, low structure carbon black made by the thermal decomposition of natural gas, coke oven gas, or liquid hydrocarbons in the absence of air or flames. Its use in the United States in 1989 was estimated at about 54–68 million kg or about 4% of total consumption. Although at one time, based on cheap natural gas, thermal black was the least expensive of the regular rubber-grade blacks, it is today the most expensive. It is used in rubber and plastics applications for its unique properties of low hardness, high extensibility, low compression set, low hysteresis, and excellent processing. Its main uses are in O-rings and seals, hose, tire innerliners, V-belts, other mechanical goods, and in cross-linked polyethylene for electrical cables.

The thermal black process dates from 1922. The process is cyclic using two refractory-lined cylindrical furnaces or generators about 4 m in diameter and 10 m high. During operation, one generator is being heated with a near stoichiometric ratio of air and off-gas from the make generation whereas the other generator, heated to an average temperature of 1300°C, is fed with natural gas. The cycle between black production and heating is five minutes alternating between generators, resulting in a reasonably continuous flow of product and off-gases to downstream equipment. The effluent gas from the make cycle, which is about 90% hydrogen, carries the black to a quench tower where water sprays lower the temperature before entering the bag filter. The effluent gas is cooled and dehumidified in a water scrubber for use as fuel in the heating cycle. The collected black from the filters is conveyed to a magnetic separator, screened, and hammer-milled. It is then bagged or pelletized. The pelletized form is bagged or sent to bulk

loading facilities. The yield is about 45% of the total carbon content of the process gas with an energy utilization of 2 × $10^8$ J/kg (0.85 × $10^5$ Btu/lb).

## ACETYLENE BLACK PROCESS

The high carbon content of acetylene (92%) and its property of decomposing exothermically to carbon and hydrogen make it an attractive raw material for conversion to carbon. Acetylene black is made by a continuous decomposition process at an atmospheric pressure of 800–1000°C in water-cooled metal retorts lined with refractory. The process consists in feeding acetylene into the hot reactors. The exothermic reaction is self-sustaining and requires water cooling to maintain a constant reaction temperature. The carbon black-laden hydrogen stream is then cooled followed by separation of the carbon from the hydrogen tail gas. The tail gas is either flared or used as fuel. After separation from the gas stream acetylene black is very fluffy with a bulk density of only 19 kg/$m^3$ (1.2 lb/$ft^3$). It is difficult to compact and resists pelletization. Commercial grades are compressed to various bulk densities up to 200 kg/$m^3$ (12.5 lbs/$ft^3$).

Acetylene black is very pure with a carbon content of 99.7%. It has a surface area of about 65 $m^2$/g, an average particle diameter of 40 nm, and a very high but rather weak structure with a DBPA value of 250 mL/100 g. It is the most crystalline or graphitic of the commercial blacks. These unique features result in high electrical and thermal conductivity, low moisture absorption, and high liquid absorption.

A significant use of acetylene black is in dry cell batteries where it contributes low electrical resistance and high capacity. In rubber it gives electrically conductive properties to heater pads, tapes, antistatic belt drives, conveyor belts, and shoe soles. It is also useful in electrically conductive plastics such as electrical magnetic interference (EMI) shielding enclosures. Its contribution to thermal conductivity has been useful in rubber curing bags for tire manufacture. Production capacity for acetylene black in the United States in 1989 was 2.07 million kg from a single plant.

## LAMPBLACK PROCESS

The lampblack process has the distinction of being the oldest and most primitive carbon black process still being practiced. The ancient Egyptians and Chinese employed techniques similar to modern methods collecting the lampblack by deposition on cool surfaces. Basically, the process consists of burning various liquid or molten raw materials in large, open, shallow pans 0.5 to 2 m in diameter and 16 cm deep under brick-lined flue enclosures with a restricted air supply. The smoke from the burning pans passes through low velocity settling chambers from which the carbon black is cleared by motor-driven ploughs. In more modern installations the black is separated by cyclones and filters. By varying the size of the burner pans and the amount of combustion air, the particle size and surface area can be controlled within narrow limits. Lampblacks have similar properties to the low area oil-furnace blacks. A typical lampblack has an average particle diameter of 65 nm, a surface area of 22 $m^2$/g, and a DBPA of 130 mL/100 g. Production is small, mostly in Western and Eastern Europe. Its main use is in

paints, as a tinting pigment where blue tone is desired. In the rubber industry lampblack finds some special applications.

### IMPINGEMENT (CHANNEL, ROLLER) PROCESS BLACKS

From World War I to World War II the channel black process made most of the carbon black used worldwide for rubber and pigment applications. The last channel black plant in the United States was closed in 1976. Operations still exist and are even being expanded in Europe. The demise of channel black was caused by environmental problems, cost, smoke pollution, and the rapid development of oil-furnace process grades that were equal or superior to channel black products particularly for use in synthetic rubber tires.

The name channel black came from the steel channel irons used to collect carbon black deposited by small natural gas flames impinging on their surface iron channels. Highly aromatic anthracene oils are used as raw material instead of natural gas. The black is scraped off the rollers, and the off-gases from the steel box enclosed rollers are passed through bag filters where additional black is collected. About half of the black is deposited on the rollers. The purified exhaust gases are vented to the atmosphere. The oils used in this process are high boiling and must be vaporized and conveyed to the large number of small burners by means of a combustible carrier gas. Yield of rubber-grade black is 60% and 10–30% for high quality color grades.

The characteristics of roller process impingement blacks are basically similar to those of channel blacks. They have an acidic pH, a volatile content of about 5%, surface area of about 100 $m^2/g$, and an average particle diameter of 10–30 nm. The smaller particle size grades are used as color (pigment) blacks, and the 30-nm grade is used in rubber.

### Characterization and Test Methods

Carbon blacks differ in particle or nodule size, surface area, aggregate size, and aggregate morphology. Surface activity is also a factor in performance, but this feature has been difficult to define or measure. The ultimate dispersible units are aggregates. Aggregate size distribution and morphology determine such properties as surface area, dibutyl phthalate absorption (DBPA), and testing strength. A complete review of the physicochemical characterization of carbon black has been published (21).

**Particle Size.**   The electron microscope is the universally accepted instrument for measuring particle size, aggregate size, and aggregate morphology. Typical electron micrographs of rubber-grade carbon blacks are shown in Figure 11. The grades are classified according to the ASTM D1765 system (2). The first letter N represents a normal rate of cure in rubber, and the first digit represents the average particle size of the carbon black. The last two digits are arbitrarily assigned. Thus N330 is a normal curing grade with a particle diameter range of 26 to 30 nm.

Particle size measurements are made from a negative enlarged to 100,000 diameters (29). Automated image analyzers provide measurements of a variety of
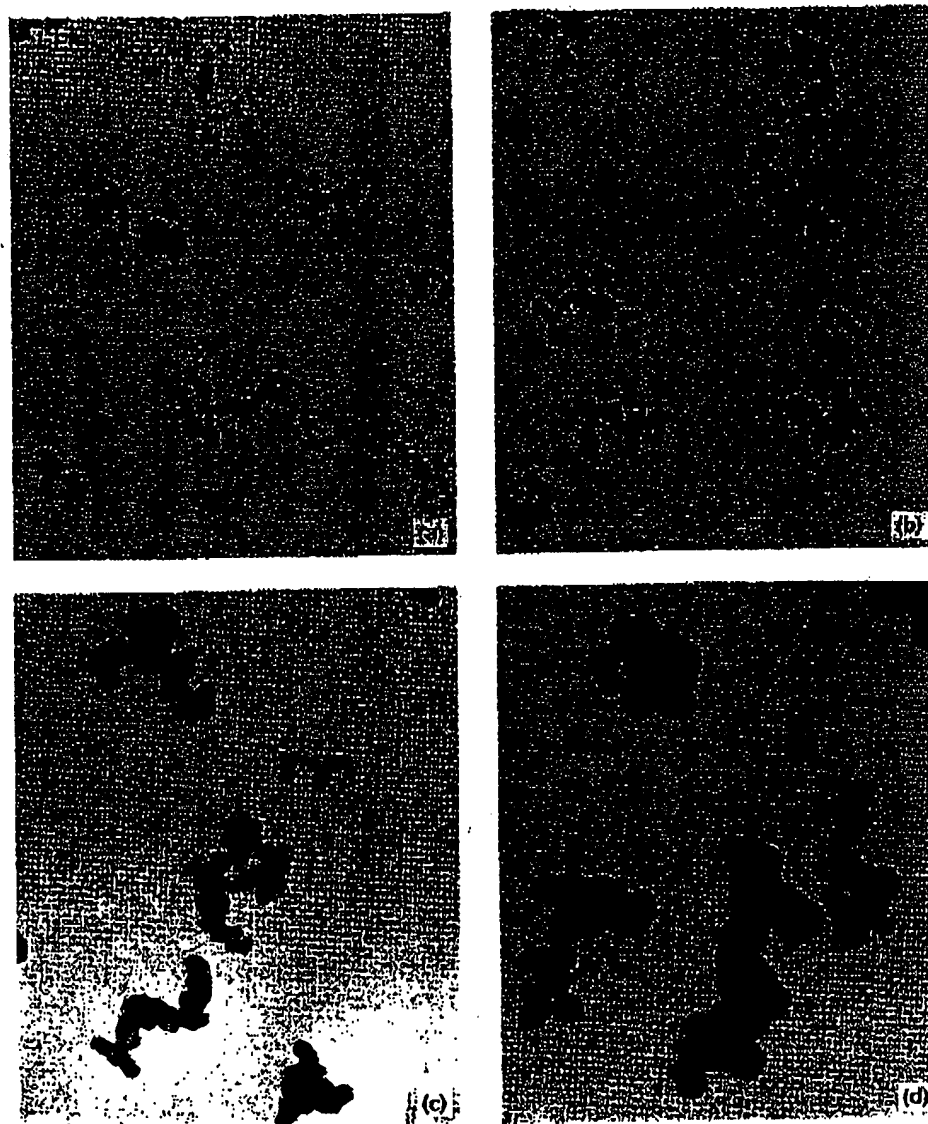
**Fig. 11.** Electron micrographs of rubber-grade carbon blacks where (a) is N110, (b) is N220, (c) is N550, and (d) is N762.

particle and aggregate parameters. Surface areas can be calculated from electron microscope measurements. These are in satisfactory agreement with surface areas determined by nitrogen adsorption measurements. Special pigment blacks and blacks used for electrical conductivity are highly porous, and the surface areas calculated from their particle diameters are very much smaller than those calculated from gas absorption.

**Surface Area.** The most important features influencing the performance of carbon blacks are aggregate size and surface area. Surface area is measured by gas- and liquid-phase adsorption techniques, and depends on the amount of adsorbate required to form a surface monolayer. If the area occupied by a single-adsorbate molecule is known, a simple calculation will yield the surface area. A low temperature nitrogen absorption method, based on the original method of

Brunauer, Emmett, and Teller (BET) (30), has been adopted by ASTM as standard method D3037-86 (2).

Liquid-phase adsorption methods are widely used for quality control and specification purposes. The adsorption of iodine from potassium iodide solution is the standard ASTM method D1510-83 (2). The surface area is expressed as the iodine number whose units are milligrams of iodine adsorbed per gram of carbon. It is quite fortuitous that the values of iodine numbers turn out to be about the same as the values for surface areas in square meters per gram by nitrogen adsorption for nonporous carbon blacks.

· Another standard industry method for surface area is based on the adsorption of cetyltrimethylammonium bromide (CTAB) from aqueous solution. This is ASTM method D3765-85 (2). This method measures the specific surface area of ʼcarbon black exclusive of the internal area contained in micrópores that are too small to admit the large CTAB molecules. For rubber-grade nonporous blacks the CTAB method gives excellent agreement with nitrogen surface areas.

**Structure and Aggregate Morphology.**  Structure or aggregate morphology is another important characteristic that influences performance. Structure is determined by aggregate size and shape. These properties affect aggregate packing and the volume of voids in the bulk material. In liquid media structure affects rheological properties such a viscosity and yield point. In rubber, viscosity, extrusion die swell, modulus, and electrical conductivity are affected by structure. For classification and quality control purposes structure is assessed by measurements of void volume, either in the bulk by density or by the absorption of a liquid such as dibutyl phthalate (DBP). The dibutyl phthalate absorption number determination is ASTM method D2414-86 (2). The void volume in the bulk is usually measured under pressure. From the bulk density under a given pressure the volume of voids per unit weight of carbon is calculated.

**Tint Strength.**  Tint strength is another industry method used for the classification of carbon blacks adopted by ASTM as D3265-85 (2). Tint strength is closely related to surface area and decreases with increasing aggregate size. It provides a rough estimate of the reinforcing potential of carbon black in rubber. In this test a small amount of carbon black is mixed with zinc oxide and an oil vehicle to produce a black or gray paste. The reflectance of this paste is measured and compared to the reflectance of a paste made with a reference black. The ratio of the reference black paste reflectance to the sample black multiplied by 100 is the tint strength.

There are many other test methods used to characterize carbon blacks for quality control and specification purposes. Table 5 lists some of these methods which, with a few exceptions, have been adopted by ASTM.

**Grades and Applications**

U.S. consumption of carbon black in 1988 by various market sectors is shown in Table 6. About 90% of total consumption is in the rubber industry and 69% for tires. About 10% is consumed for other automotive products and 11% for rubber products unrelated to the automotive industry. The automotive industry accounts

**Table 5.** Special Analytical Test Methods for Carbon Black

| Test method | Standard | Comment |
|---|---|---|
| iodine adsorption, mg/g | ASTM D1510 | amount of iodine adsorbed from aqueous solution as a measure for the specific surface area; not applicable for oxidized or highly porous carbon blacks |
| $N_2$ surface area, $m^2/g$ | ASTM D3037 | calculated from amount of adsorbed $N_2$ at liquid nitrogen temperature |
| CTAB surface area, $m^2/g$ | ASTM D3765 | amount of cetytrimethylammonium bromide adsorbed from aqueous solution as measure of specific nonporous (outer) surface area |
| aggregate dimension | ASTM D3849 | determination of aggregate dimensions (unit length, width, etc) by electron microscope image analysis |
| aggregate size distribution | | diameters of equivalent solid spheres that sediment at same rate as aggregates during centrifuging |
| DBP absorption, mL/100 g | ASTM D2414 | determination of the void volume with dibutyl phthalate in a special kneader as measure of structure |
| void volume, mL/100 g | | volume of voids from bulk density measurement under pressure |
| 24M4-DBP absorption, mL/100 g | ASTM D3493 | determination of DBP absorption after four repeated compressions at 165 MPa (24,000 psi) |
| jetness | | light absorption of a carbon black paste in linseed oil; determination by visual comparison against standard blacks or by measuring the absolute light emission |
| tint strength, % | ASTM D3265 | ability of a carbon black to darken a white pigment in a linseed oil paste; the tinting strength is the weight percentage of the standard carbon black with respect to the tested black to obtain the same gray tone; different standard white pigments and carbon black concentrations are used according to ASTM |
| volatiles, % | ASTM D1620 | weight loss when calcined at 950°C for 7 min |
| heating loss (moisture), % | ASTM D1509 | weight loss on drying at 125°C for 1 h |
| pH | ASTM D1512 | pH of an aqueous slurry of carbon black; pH is mainly influenced by surface oxides |
| extractables, % | | amount of material which can be extracted by a boiling solvent, usually toluene, in at least 8 h |
| | ASTM D3392 | light absorption–transmission of a 1,2-dichlorobenzene solution of the extracted material |

**Table 5. (Continued)**

| Test method | Standard | Comment |
|---|---|---|
| ash content, % | ASTM D1506 | amount of noncombustible material after burning the carbon black at 675°C |
| sulfur content, % | ASTM D1619 | |
| sieve residue, % | ASTM D1514 | amount of coarse impurities that cannot be purged through a testing sieve by water |
| bulk density, g/L | ASTM D1513 | measure for the densification of carbon black |
| tamped density, g/L | | similar to bulk density; however, void volume is reduced by tamping |
| pellet size distribution | ASTM D1511 | determination by means of sieve shaker |
| fines content, % | ASTM D1508 | only for pelletized blacks; percentage passing through a sieve of 125 μm (mesh) width |

for 79% of consumption. Pigment applications account for about 10% of consumption, most of this for plastics and printing inks. Western Europe consumes 74% in tires and other automotive products and almost 20% in other industrial rubber products. Pigment applications in Western Europe and Japan are 5–6% of consumption.

**Table 6. U.S. End Use Consumption of Carbon Black[a]**

| Market sector | Consumption, $10^3$ t | Percent of total, % |
|---|---|---|
| *Rubber* | | |
| tires, treads, tubes | 927 | 68.9 |
| other automotive | 132 | 9.8 |
| molded, extruded, industrial products, roofing, etc | 148 | 10.9 |
| *Total rubber* | *1207* | *89.6* |
| *Nonrubber* | | |
| plastics | 59 | 4.4 |
| printing inks | 48 | 3.6 |
| paint | 9 | 0.7 |
| paper | 7 | 0.5 |
| other | 16 | 1.2 |
| *Total nonrubber* | *139* | *10.4* |

[a]1988.

**Rubber Goods.**  A selected list of typical properties, taken from ASTM D1765 of rubber-grade carbon blacks (2), is shown in Table 7. In addition to the assigned ASTM N-numbers, the list includes the old letter designations, pour

densities, structure (DBPA), surface areas, and tint data. The structure/area relationships of these grades, called the carbon black spectrum, is illustrated in Figure 12, which shows a diagram of DBPA values versus the nitrogen surface areas. Closely related grades are easily distinguished. A broad range of structure is available in the N700-N600 and N300 range of surface areas. Table 8 lists the principal rubber grades by their N-number classification, general rubber properties, and typical uses. The behavior of different grades is dominated mainly by surface area and structure (DBPA). High surface area produces high reinforcement as reflected in high tensile and tear strengths, high resistance to abrasive wear, higher hysteresis, and poorer dynamic performance. A present day challenge to carbon black technologists is to optimize the balance between tire wear and tire hysteresis or the rolling resistance. Some progress on this problem has been made by using new furnace designs and other process variables that broaden the aggregate size distributions and lower the tint strength while maintaining surface area, structure, and reinforcement (31,32).

**Fig. 12.** Rubber grades carbon black spectrum.
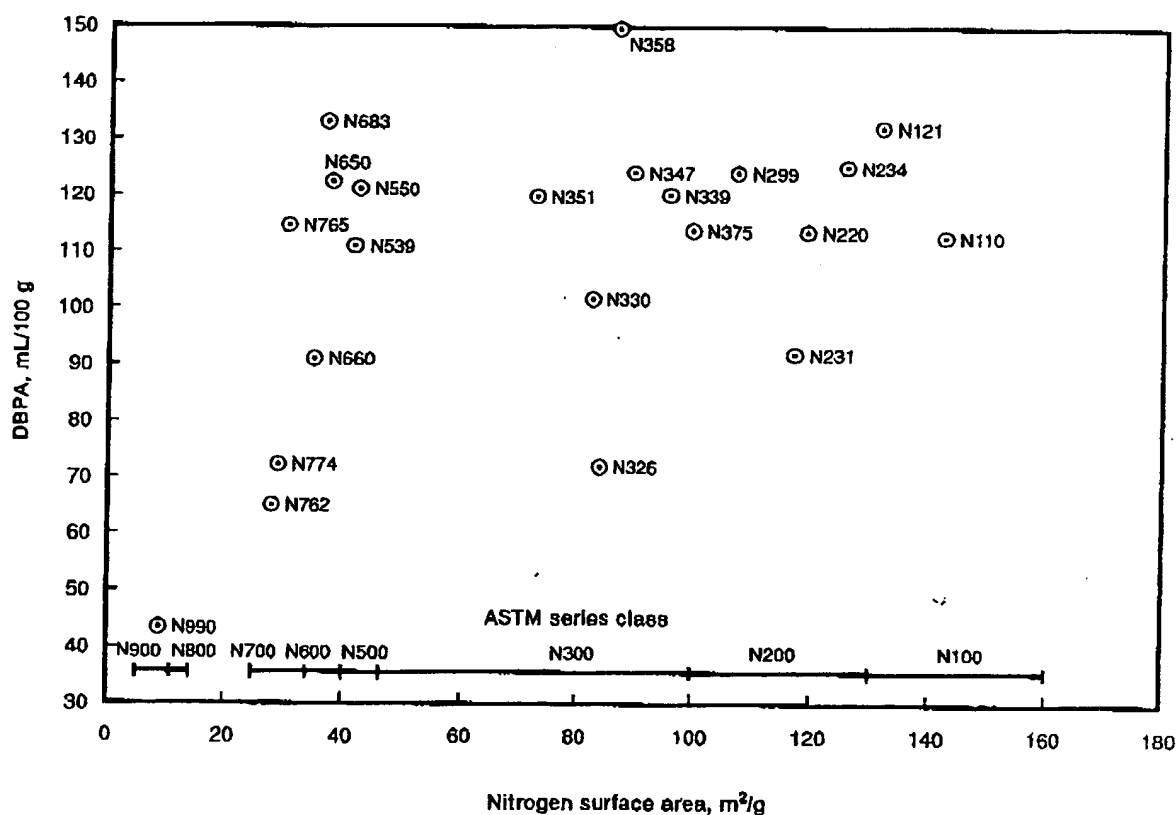
The consumption of the various carbon black grades can be divided into tread grades for tire reinforcement and nontread grades for nontread tire use and other rubber applications. Table 9 shows the distribution of production of types for these uses. In the United States 55% production is for tread grades. In Western Europe tread-grade production is 64%, and in Japan it is 60%.

**Table 7. Typical Properties Rubber-Grade Carbon Blacks[a]**

| ASTM designation | Former industry designation[b] | I₂ absorption number (D1510), g/kg | DBPA[c] (D2414), mL/100 g | DBPA[c] (compressed sample) (D3493), mL/100 g | CTAB[d] surface area (D3765), m²/g | Nitrogen surface area (D3037), m²/g | Tinting strength (D3265) | Pour density (D1513), kg/m³ |
|---|---|---|---|---|---|---|---|---|
| N110 | SAF | 145 | 112 | 98 | 126 | 143 | 124 | 335 |
| N121 | SAF-HS | 121 | 132 | 112 | 121 | 132 | 121 | 320 |
| N220 | ISAF | 121 | 114 | 100 | 111 | 119 | 115 | 345 |
| N231 | ISAF-LM | 121 | 92 | 86 | 108 | 117 | 117 | 390 |
| N234 | ISAF-HS | 120 | 125 | 100 | 119 | 126 | 124 | 320 |
| N299 | ISAF-HS | 108 | 124 | 105 | 104 | 108 | 113 | 335 |
| N326 | HAF-LS | 82 | 72 | 69 | 83 | 84 | 112 | 465 |
| N330 | HAF | 82 | 102 | 88 | 83 | 83 | 103 | 375 |
| N339 | HAF-HS | 90 | 120 | 101 | 95 | 96 | 110 | 345 |
| N347 | HAF-HS | 90 | 124 | 100 | 88 | 90 | 103 | 335 |
| N351 | HAF-HS | 68 | 120 | 97 | 74 | 73 | 100 | 345 |
| N358 | HAF-HS | 84 | 150 | 112 | 88 | 87 | 99 | 290 |
| N375 | HAF-HS | 90 | 114 | 97 | 98 | 100 | 115 | 345 |
| N539 | FEF | 43 | 111 | 84 | 41 | 41 | 0 | 385 |
| N550 | FEF | 43 | 121 | 88 | 42 | 42 | 0 | 360 |
| N650 | GPF-HS | 36 | 122 | 87 | 38 | 38 | 0 | 370 |
| N660 | GPF | 36 | 90 | 75 | 35 | 35 | 0 | 425 |
| N683 | GPF-HS | 35 | 133 | 0 | 39 | 37 | 0 | 335 |
| N762 | SRF | 27 | 65 | 57 | 29 | 28 | 0 | 505 |
| N765 | SRF-HS | 31 | 115 | 86 | 33 | 31 | 0 | 375 |
| N774 | SRF | 29 | 72 | 62 | 29 | 29 | 0 | 495 |
| N990 | MT | 0 | 43 | 40 | 9 | 9 | 0 | 0 |

[a]ASTM D1765.
[b]SAF = super abrasion furnace; ISAF = intermediate super abrasion furnace; HAF = high abrasion furnace; FEF = fast extrusion furnace; GPF = general purpose furnace; SRF = semireinforcing furnace; MT = medium thermal; HS = high structure; LS = low structure; LM = low modulus.
[c]Dibutyl phthalate [84-74-2] absorption.
[d]Cetyl trimethylammonium bromide [57-09-0].

**Table 8.** Applications of Principal Rubber-Grade Carbon Blacks

| Designation | General rubber properties | Typical uses |
|---|---|---|
| N110, N121 | high abrasion resistance | special tire treads, airplane, off-the-road racing |
| N220, N299, N234 | high abrasion resistance, good processing | passenger, off-the-road, special service tire treads |
| N339, N347, N375, N330 | high abrasion resistance, easy processing, good abrasion resistance | standard tire treads, rail pads, solid wheels, mats, tire belt, sidewall, carcass retread compounds |
| N326 | low modulus, good tear strength, good fatigue, good flex cracking resistance | tire belt, carcass, sidewall compounds, bushings, weather strips, hoses |
| N550 | high modulus, high hardness, low die swell, smooth extrusion | tire innerliners, carcass, sidewall, innertubes, hose, extruded goods, v-belts |
| N650 | high modulus, high hardness, low die swell, smooth extrusion | tire innerliners, carcass, belt, sidewall compounds, seals, friction compounds, sheeting |
| N660 | high modulus, high hardness, low die swell, smooth extrusion | carcass, sidewall, bead compounds, innerliners, seals, cable jackets, hose, soling, EPDM compounds |
| N762 | high elongation and resilience, low compression set | mechanical goods, footwear, innertubes, innerliners, mats |

**Table 9.** Carbon Black Production[a] by Grade, $10^3$ t

| | United States | Western Europe | Japan |
|---|---|---|---|
| N100 | 35 | 28 | 37.1 |
| N200 | 158 | 161 | 118 |
| N300 | 555 | 528 | 300 |
| *Total tread grades* | *748* | *717* | *418* |
| percent | 55.2 | 63.8 | 59.5 |
| N500 | 120 | 153 | 136 |
| N600 | 326 | 137 | 87 |
| N700 | 129 | 103 | 29 |
| N900 (thermal) | 23 | | 9 |
| *Total nontread grades* | *598* | *393* | *261* |
| percent | 44.1 | 35.0 | 37.1 |
| other grades | | | |
| acetylene | 9.1 | 14 | 24 |
| *Total carbon black* | *1355* | *1124* | *703* |

[a]1988.

**Special-Grade Carbon Blacks.** In 1988 over 10% of U.S. consumption of carbon black was for nonrubber applications, ie, special blacks. In Europe and Japan about 5% is consumed for these uses. Most of the special black grades are manufactured by methods to meet specific product specifications required for their end uses. They sell for a higher average price than the rubber grades. These markets have been growing at an average annual rate twice that of the rubber black grades. Of increasing importance in recent years have been applications in plastics to improve weathering resistance and to impart antistatic and electrically conductive properties.

About 42% of special blacks are used in plastics, 35% in printing inks, 7% in paper, and 16% in miscellaneous applications. News inks account for most of the printing ink market. Electrical applications have been taking an increasing share of the plastics market. Medium and high color grades, in their normal and surface-oxidized versions, are used in enamels, lacquers, and plastics for their extreme jetness. Typical properties of special grades of furnace blacks are listed in Table 10. The list is divided into normal furnace grades and surface oxidized grades. Increased surface oxidation decreases viscosity, improves dispersion, and increases the flow behavior in many liquid systems. The volatile content is an indication of the degree of surface oxidation. To improve dispersion and flow, special blacks generally are produced at lower structural (DBPA) and bulk density values than rubber-grade carbon blacks.

Table 11 lists the types and applications of special pigment-grade carbon blacks. Included in this list are thermal black and lampblack. Over 40 special black grades have been developed based on the furnace process having a broad range of surface areas, from 20 $m^2$/g to over 1500 $m^2$/g. The lower surface area products are used in printing inks and tinting. The high area, more expensive products find use in high color enamels and lacquers.

**Electrically Conductive Grades.** An important application of carbon black is to produce electrically conductive and antistatic polymer composites. These applications include antistatic carpet backing and floor tile, electrical heating elements, high voltage cable semiconductive shields, video tapes and disks, and EMI shielding. The electrical conductivity of bulk carbon black under compression is in the range of 0.02 to 0.5 ohm·cm. The conductivity of conductive carbon black-filled rubber and plastics is in the range of 1 to $10^8$ ohm·cm. There is no clear relationship between bulk black conductivity and compound conductivity. The main variable determining compound conductivity is the carbon black concentration. At high enough concentrations all carbon blacks can produce compound resistivities of about 1.0 ohm·cm. For superconductive carbon black this concentration is 7-8% and for thermal black the required concentration is 65-70%. Figure 13 shows the concentration/resistivity relationships of selected carbon blacks covering the complete range of rubber and conductive grades (33). It can be seen that there is a critical concentration for each grade of carbon black above which the resistivity drops precipitously. This is often referred to as the percolation concentration.

The main carbon black characteristics determining its conductive behavior are surface area, aggregate morphology, and degree of graphitization or crystallinity. The high conductivity of acetylene black is attributed to its highly developed structure and its crystallinity. High conductivity furnace-grade blacks have

**Table 10. Furnace Process Special Grades for Pigment Applications in Inks, Plastics, Paints, and Paper**

| Industry classification | $N_2$ surface area, $m^2/g$ | Particle diameter, nm | DBPA[a], mL/100 g | | Bulk density, g/L | | Nigrometer[b] index | Tinting strength | Volatile, % | pH |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Fluffy | Pellets | Fluffy | Pellets | | | | |
| high color | 250–300 | 14–15 | 70–75 | 60–65 | 50–300 | 400–550 | 65–76 | 117–124 | 1.2–2.0 | 7–10 |
| medium color | 150–220 | 16–24 | 47–122 | 46–117 | 130–300 | 390–550 | 74–78 | 118–124 | 1.0–1.5 | 8–10 |
| regular color | 45–140 | 20–37 | 42–125 | 42–124 | 176–420 | 350–600 | 84–93 | 73–119 | 0.9–1.5 | 6–10 |
| low color | 25–45 | 41–76 | 71 | 64–120 | 256 | 352–512 | 94–99 | 48–69 | 0.6–0.9 | 8–10 |
| | | | | | *Surface oxidized grades* | | | | | |
| high color | 400–600 | 10–20 | 121 | 105 | | | 64 | 100–135 | 8.0–9.5 | 2.0–3.3 |
| medium color (long flow) | 100–38 | 23–24 | 49–60 | 55 | 240–360 | 530 | 83–84 | 112–135 | 3.5–5.0 | 2.5–4.0 |
| medium color (medium flow) | 96–110 | 25 | 49–72 | 70 | 225–360 | 480 | 84 | 112–114 | 2.5–3.5 | 4.0–4.5 |
| low color | 30–40 | 50–56 | 48–93 | | 260–500 | | 92–100 | 64 | 3.5 | 3.0 |

[a]Dibutyl phthalate absorption.
[b]A method for measuring the diffuse reflectance from a black paste with a black tile standard. The low numbers represent the jettest or most intense black grades.

**Table 11. Types and Applications of Special Pigment Grades of Carbon Blacks**

| Type | Surface area, $m^2/g$ | DBPA[a], mL/100 g | Volatile content, % | Uses |
|------|------|------|------|------|
| *Normal grades* | | | | |
| high color | 230–560 | 50–120 | 2 | high jetness for alkyl and acrylic enamels, lacquers, and plastics |
| medium color | 220–220 | 70–120 | 1–1.5 | medium jetness and good dispersion for paints and plastics; ultraviolet and weathering protection for plastics |
| regular color | 80–140 | 60–114 | 1–1.5 | for general pigment applications in inks, paints, plastics, and paper; gives ultraviolet protection in plastics, high tint, jetness, gloss, and dispersibility in inks and paints |
| | 46 | 60 | 1.0 | good tinting strength, blue tone, low viscosity; used in gravure and carbon paper inks, paints, and plastics |
| | 45–85 | 73–100 | 1.0 | main use is in inks; standard and offset news inks |
| low color | 25–42 | 64–120 | 1.0 | excellent tinting black-blue tone; used for inks-gravure, one-time carbon paper inks; also for paints, sealants, plastics, and cements |
| thermal blacks | 7–15 | 30–35 | <0.5 | tinting-blue tone; plastics and utility paints |
| lamp blacks | 20–95 | 100–160 | 0.4–0.9 | paints for tinting-blue tone |
| *Surface oxidized grades* | | | | |
| high color | 400–600 | 105–121 | 8.0–9.5 | used for maximum jetness in lacquers, coatings, plastics, fibers, record disks |
| medium color, long flow | 138 | 55–60 | 5 | used in lithographic, letterpress, carbon paper, and typewriter ribbon inks; high jetness, excellent flow, low viscosity, high tinting strength, gloss, and good dispersability |
| medium color, long flow | 96 | 70 | 2.5 | used for gloss printing and carbon paper inks; excellent jetness, dispersibility; tinting strength, and gloss in paints |
| low color | 30–40 | 48–93 | 3.5 | used for tinting where flooding is a problem; easy dispersion |

[a]Dibutyl phthalate absorption.

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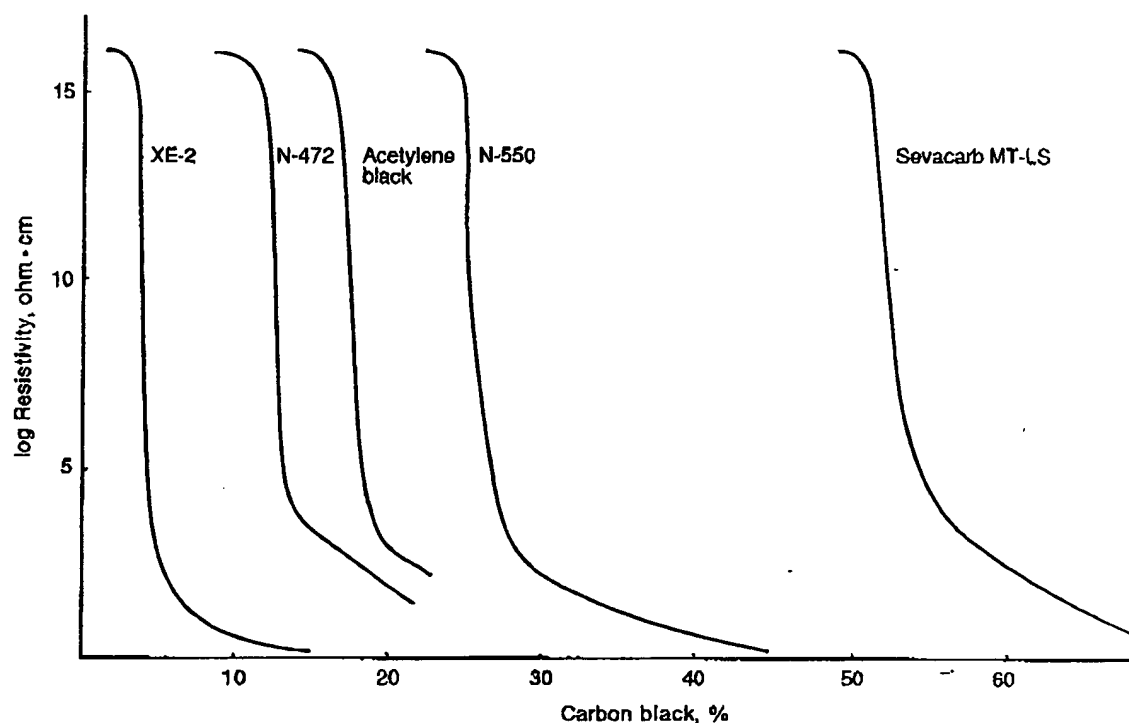


**Fig. 13.**   Electrical resistivity versus carbon black concentration.

very high surface areas and structures (DBPA). Superconductive blacks, by-products of synthesis gas manufacture, have very high surface areas, highly developed structures, and a high degree of crystallinity.

The effect of surface area on conductivity was shown for channel-grade blacks in 1949 (34) and the surface area relationship to conductivity for furnace blacks in 1954 (35). High surface area is associated with increasing surface roughness and internal porosity rather than decreased particle or nodule size. Because of the decreased density of the aggregates resulting from the porosity of high surface area conductive blacks, they possess a larger number of aggregates per unit weight. At a given weight concentration, closer packing of aggregates increases conductivity. Crystallinity increases with high porosity contributing to high conductivity. The crystallinity increase results from the burnout of the more amorphous regions of the aggregate during manufacture.

The mechanism of electrical conduction in composites occurs by a process of electron tunneling through the polymer phase (36). Electrons tunnel from the black aggregates to their nearest neighbor. The resistivity of vulcanizates is a function of the average distance between aggregates (37). In addition to carbon black concentration, this gap distance depends on particle size, surface area, and aggregate morphology.

There are a number of publications on the properties and applications of electrically conductive carbon blacks (38–40). Figure 14 shows the electron micrographs of two grades of electrically conductive carbon blacks. The furnace blacks have the particle size of N200-N300 types. Their high surface areas indicate high internal porosity. Table 12 shows typical data and uses for eight electrically

conductive grades of carbon black and by-product carbons. The large differences between the nitrogen surface areas and the areas measured by cetyltrimethyl-ammonium bromide (CTAB) absorption are because of internal porosity. The CTAB molecules are so large that they do not penetrate the pores available to the nitrogen molecules. The large, bulky aggregates, the high porosities, and low aggregate densities of the electrical grades produce high DBPA values, much larger than for normal furnace blacks.
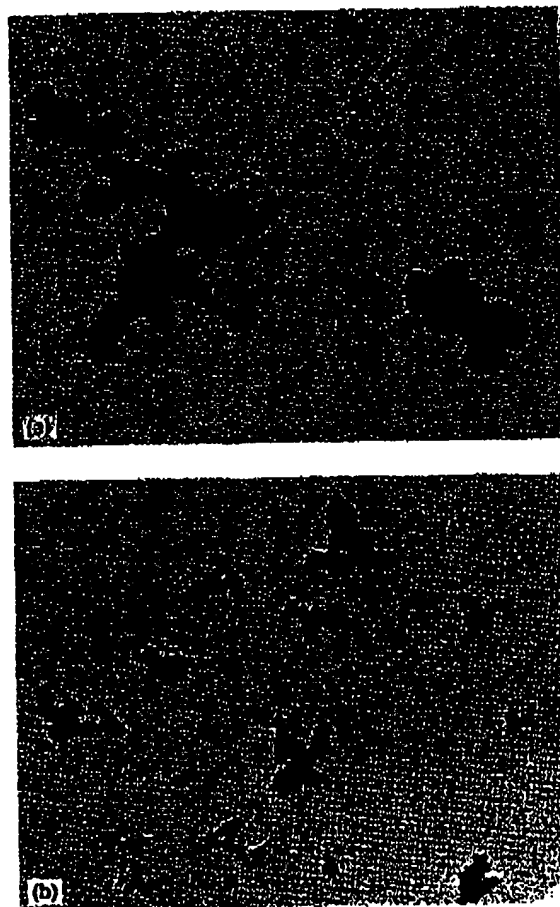


Fig. 14.    Electron micrographs of electrically conductive grades of carbon black where (a) is Vulcan XC-72 (Cabot) (100,000 ×) and (b) is Vulcan P (Cabot) (100,000 ×).

## Carbon Black Manufacture and Market

**Manufacturers and Productions.**   The consumption of carbon black in the United States reached a peak of 1,506,000 t during the beginning of the oil crisis in 1973. Then consumption decreased to 1,210,000 t in 1989. A number of events have contributed to decreased consumption by the rubber and tire industries including tire radialization, increased tire mileage, downsizing of tires, and increased imports of foreign cars. The negative influence of these events have pretty much run their course, and during the last 10 years there has been a modest growth in

**Table 12.** Typical Data and Uses for Electrically Conductive Grades of Carbon Blacks

| Type | Particle diameter, nm | $N_2$ Surface area, m²/g | CTAB Surface area, m²/g | DBPA[a] mL/100 g | Tinting strength, D3265 | Uses |
|---|---|---|---|---|---|---|
| acetylene black | 42 | 64 | | 300 | 52 | high voltage semiconductive shields, conductive rubber, and plastics |
| conductive furnace (CF)N293 | 22 | 145 | 114 | 100 | 117 | conductive rubber and plastics, carpet backing |
| conductive furnace (CF)N742 | 22 | 270 | 145 | 178 | 82 | conductive and antistatic rubber and plastics products |
| superconductive furnace (SCF) | | 1475 | | 330 | 163 | electromagnetic interference shielding (EMI) compounds, videodisks, tapes, etc |
| | | 1000 | | 245 | | |
| synthesis gas by-product carbon | 30 | 800 | | 365 | 124 | EMI, videodisks, PTC[b] compounds (for heating tapes) |
| | | 1000 | 620 | 400 | | |
| | | 1250 | | 495 | | |

[a]Dibutyl phthalate absorption.
[b]PTC = positive temperature coefficient.

carbon black production. Production for the period 1973–1989 is shown in Figure 15.
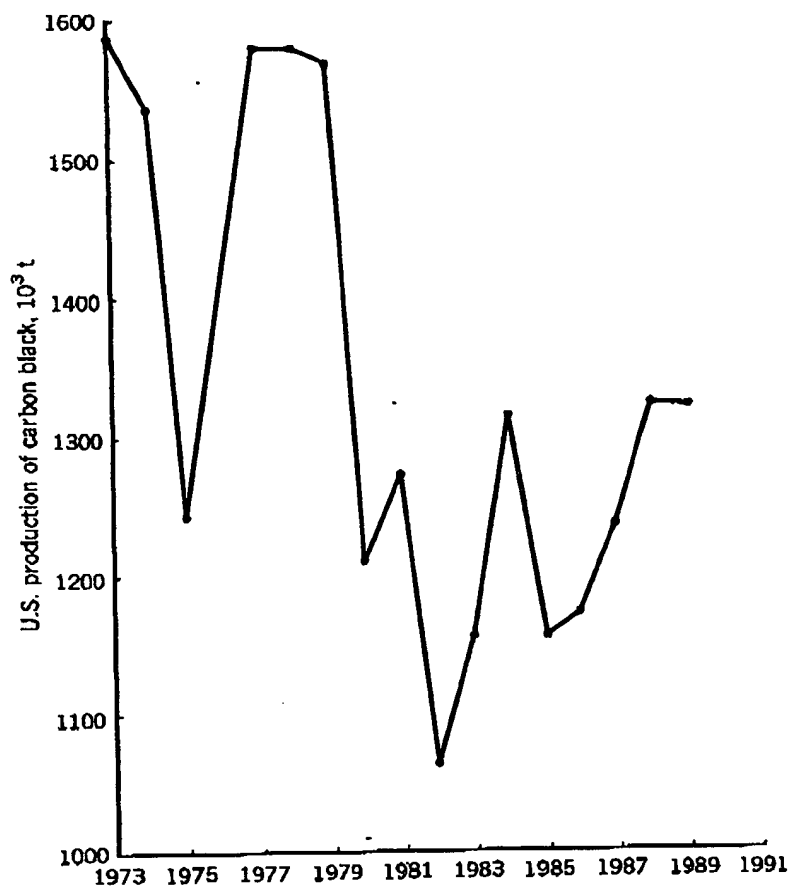
Fig. 15. U.S. production of carbon black (1973–1989).

The shrinkage in demand has resulted in a restructuring of the carbon black industry. Several of the principal multinational oil companies have left the business including Ashland, Cities Service Co., Phillips, and Conoco. Some plants have changed ownership. In the United States this has increased the production capacities of Degussa, Sid Richardson, and Huber. Today's U.S. industry consists of six principal producers. Rated capacities of the six U.S. manufacturers is shown in Table 13. Cabot Corp. and Columbian Chemicals are the leading producers, followed by Degussa, Sid Richardson, J. M. Huber Corp., and Witco. A survey of the future markets and present structure of the carbon black industry has been presented (1).

World carbon black rated capacities are shown in Table 14. North America has the largest capacity. Europe, Southeast Asia, and Russia/Eastern Europe have about equal capacities and Africa and the Middle East have only small production. The growth areas are predicted to be Southeast Asia and the Russia/Eastern Europe markets. The capacities for certain areas such as China and Russia/Eastern Europe should be taken as rough estimates.

**Table 13.** U.S. Carbon Black Manufacturers Nameplate Capacities, 1988

| Manufacturers | Capacity $10^3$ t | U.S. capacity, % |
|---|---|---|
| Cabot Corp. | | |
| Franklin, La. | 153 | |
| Pampa, Tex. | 32 | |
| Parkersburg, W.Va. | 83 | |
| Ville Platte, La. | 126 | |
| *Total* | *394* | 25 |
| Columbian Chemicals | | |
| El Dorado, Ark. | 75 | |
| North Bend, La. | 121 | |
| Hickok, Kans. | 38 | |
| Moundsville, W.Va. | 82 | |
| *Total* | *316* | 20 |
| Degussa | | |
| Arkansas Pass, Tex. | 82 | |
| Ivanhoe, La. | 100 | |
| Belpre, Ohio | 55 | |
| *Total* | *237* | 15 |
| Sid Richardson Co. | | |
| Addis, La. | 62 | |
| Big Spring, Tex. | 57 | |
| Borger, Tex. | 125 | |
| *Total* | *244* | 15.5 |
| J. M. Huber Corp. | | |
| Orange, Tex. | 62 | |
| Baytown, Tex. | 102 | |
| Borger, Tex.—Furnace | 57 | |
| Thermal | 23 | |
| *Total* | *244* | 15.5 |
| Witco Corp. | | |
| Phenix City, Ala. | 25 | |
| Ponca City, Okla. | 68 | |
| Sunray, Tex. | 46 | |
| *Total* | *139* | 8.8 |
| *Total U.S. capacity* | *1574* | |

## Product Safety

The safety aspects of carbon black have been the subject of a number of reviews and articles (41–43). The manufacture of carbon results in trace amounts of organic and inorganic impurities. These impurities have been suspected of causing potential health problems. Of particular concern have been the salts of toxic metals and adsorbed polynuclear aromatic hydrocarbons (PNAs). A few of the polyaromatic hydrocarbons are known to be mutagens and/or animal carcinogens. The solvent extract of furnace blacks is in the range of 300 to 2000 ppm (0.03–0.20%). Most of this extract consists of 10–15 organic compounds, the

**Table 14.** World Carbon Black Capacities by Region and Country, 1988

| Region | Number of plants | Estimated capacity, $10^3$ t |
|---|---|---|
| North America | | |
| United States | 22[a] | 1565[a] |
| Canada | 3[a] | 182 |
| Mexico | 2 | 158 |
| *Total* | *27* | *1095* |
| South America | | |
| Argentina | 1 | 48 |
| Brazil | 3 | 199 |
| Colombia | 2 | 36 |
| Peru | 1 | 8 |
| Venezuela | 1 | 40 |
| *Total* | *8* | *331* |
| Europe | | |
| Great Britain | 2 | 140 |
| France | 3 | 239 |
| Germany | 5 | 385 |
| The Netherlands | 2 | 120 |
| Italy | 3 | 191 |
| Portugal | 1 | 21 |
| Spain | 3 | 104 |
| Sweden | 1 | 33 |
| *Total* | *20* | *1233* |
| Australia/South East Asia | | |
| Australia | 2 | 76 |
| India | 7 | 153 |
| China[b] | 30–45 | 500 |
| Japan | 12 | 766 |
| South Korea | 3 | 170 |
| Malaysia | 1 | 23 |
| Pakistan | 1 | 10 |
| Philippines | 1 | 15 |
| Taiwan | 1 | 53 |
| Thailand | 1 | 20 |
| *Total* | *32* | *1786* |
| Africa | 2 | 75 |
| Middle East | | |
| Iran | 1 | 15 |
| Turkey | 1 | 35 |
| *Total* | *2* | *50* |
| Russia/Eastern Europe | | |
| Russia[b] | 14 | 1300 |
| Yugoslavia | 1 | 36 |
| Poland | | 58 |
| Romania | | 130 |
| Czechoslovakia | | 64 |
| *Total* | | *1588* |
| *Total world capacity* | | *6968* |

[a]Includes one thermal black plant (capacity, 25,000 t).
[b]Estimate.

majority of which are not genotoxic. One compound that is toxic is benzo [α] pyrene [50-32-8], BαP, often used as an indicator of potential hazard. BαP ranges from 0 to 50 ppm and is less than one percent of the total extract. There have been a number of studies initiated by the U.S. carbon black industry to examine the health effects of various commercial carbon blacks and their benzene extracts. Tests have been made using laboratory animals. Investigations on absorption and elution effects in stomach fluids and human blood have been conducted. Although the solvent extracts of carbon black do show toxic properties, the aqueous systems of concern in humans show no elution of BαP and no toxic properties. The BαP is believed to be so strongly absorbed on the surface of carbon black and in such high dilution that it is inactive in animal testing for carcinogenicity. Statistical studies on the frequency of cancer of long-term employees in a carbon black plant covering a period of 17 years (1939–1956) has been reported (44). There is no evidence of increased cancer risk from exposure to industrial carbon blacks. The scientific literature based on animal research as well as observations on carbon black plant employees show no evidence of detrimental health effects. Most studies of carbon black dust inhalation and intratracheal administration with animals indicate that carbon black is not carcinogenic. OSHA regulations for carbon black dust concentrations call for an average exposure level over a given time period of not more than 3.5 mg/m$^3$.

## Environmental Aspects

The carbon black industry takes extreme efforts to confine product during all stages of manufacture (45). Highly efficient bag filters are used to collect the product. After collection the fluffy carbon black is densified and pelletized to minimize dusting problems during shipping and use.

The process gases from the filters consist of nitrogen, carbon monoxide, carbon dioxide, hydrogen, water, small amounts of hydrogen sulfide, and other sulfur- and nitrogen-containing gases. In the past the process gases have been flared. Process gas is used as a fuel for in-plant heat needs, and where local conditions warrant, it may be burned to generate steam or power.

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## DIAMOND, NATURAL

Naturally occurring diamond is a relatively rare polymorphic form of carbon characterized by a three-dimensional arrangement of tetrahedrally coordinated carbon atoms. Both natural and synthesized diamond [7782-40-3] have the highest hardness of all known materials, the highest thermal conductivity at room temperature, a high refractive index and optical dispersion, a low thermal expansion, and a relatively high inertness to chemical attack. This unique combination of properties permits diamond to be foremost in certain applications: as a highly prized gemstone; industrially as an important abrasive material unsurpassed in certain cutting, drilling, sawing, machining, grinding, and polishing operations for many materials; and in electronic and optical applications as a heat sink and window material, respectively.

### Occurrence and Exploration

Diamonds were first discovered in ancient times in India and Borneo and later in Brazil in 1670 in alluvial deposits where water had sorted minerals on the basis of density and toughness. This type of tumbling often concentrates the better quality crystals such as those found in the ocean off the west coast of Africa. Exploration can be done by stream panning or drilling in conjunction with a search for the heavy mineral assemblages that accompany diamond. Alluvial deposits account for about 40% of the diamond found in primary sources.

Upstream exploration has sometimes led to the discovery of the primary source of alluvial stones, namely, kimberlite "pipes." These structures of igneous origin are the principal source of natural diamonds, and there are over 1000 occurrences of them in the world. Only a small number contain a high enough concentration of diamonds to warrant mining. Even in successful mining operations the ratio of diamond to the gangue that has to be removed and crushed is of the order of one part in a million or even less, of which the proportion of gem